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THE UNIVERSITY OF ALBERTA

DITHIOLATE COMPLEXES OF THE EARLY TRANSITION METALS

by

JOEL MARTIN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

AND RESEARCH IN PARTIAL FULFILMENT OF THE

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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled DITHIOLATE COMPLEXES OF THE EARLY TRANSITION METALS submitted by JOEL MARTIN in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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ABSTRACT

Metal dialkylamides have been used to prepare complexes of the type $[R_4E]_{(6-x)}ML_3$ where R_4E is a tetraalkylammonium or tetraphenylarsonium ion, L=benzene-1,2-dithiol, toluene-3,4-dithiol or o-mercaptophenol (for M=Ti, Zr, Hf, Nb, and Ta), L=1,2-dihydroxybenzene (for Ti and Hf), L=naphthalene-1,8-dithiol (for Ti, Zr, and Hf), and x=4 (for Ti, Zr and Hf) or x=5 (for Nb and Ta). The complexes were prepared as Li or Na salts according to the general equation:

$$M(NR_2)_x + (6-x)NaHL + (x-3)H_2L \xrightarrow{THF} Na_{(6-x)}ML_3 + xHNR_2$$

The alkali metal was then replaced by an organic cation in acetonitrile. Comparison of UV and visible spectra of the new complexes with previously isolated complexes shows that there is a shift of the lowest energy band to higher energy in the order: Ti<Zr<Hf, Nb<Ta, Mo<Nb<Zr, W<Ta<Hf. A similar shift was observed for the order $S_2C_6H_4^{2-} < OSC_6H_4^{2-} < O_2C_6H_4^{2-}$. The shifts above are consistent with spectra dominated by ligand to metal charge transfer bands. A tentative assignment of the metal-sulfur stretching frequencies

is consistent with metal-sulfur bonds becoming weaker in the same order as the spectral shifts.

A single crystal x-ray structure determination of $[(C_6H_5)_4As]$ $Ta(S_2C_6H_4)_3$ has been performed and comparison of the results with the tris(benzene-1,2-dithiolato Ti, Zr, Nb and Mo structures indicates that the proper matching of metal d-orbital energy and ligand orbital energy is important for the stabilization of trigonal prismatic geometry. The Ta complex is not trigonal prismatic, but instead two of the chelates retain nearly the trigonal prismatic configuration, while the third chelate is twisted by 37^0 about the C_2 axis of the prism. A reexamination of the structures of other tris dithiolene complexes in light of the above C_2 distortion shows that a C_2 type of distortion is a better description of the structures than the usual description invoking a trigonal distortion. The Ta complex appears to represent the most pronounced example of this C_2 type of distortion.

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LIST OF ABREVIATIONS

Me = methyl

Et = ethyl

Pr^n = n-propyl

Bu = butyl

Ph = phenyl

Pr^i = isopropyl

CHAPTER 1: HISTORICAL CONSIDERATIONS

The view[1] that class a, or hard, acids should not form strong bonds to class b, or soft, bases is well illustrated in the formation of complexes between the early transition metals and ligands containing only sulfur as the donor atom. The early transition metals are good examples of hard acids due to their predominantly high oxidation states and lack of polarizable valence shell electrons. Sulfur, on the other hand, is a very soft base due to its large size and low electronegativity. Thus, according to hard and soft acid base theory, sulfur and the early transition metals should be very badly mismatched as far as bonding is concerned. As will be seen below, this prediction appears to be correct. However, it must be kept in mind that several factors are involved in determining the hardness of an acid or base, and thus it is not strictly correct to fail to distinguish between various types of sulfur donors, nor is it correct to consider all of the early transition metals as essentially the same. For example, a high negative charge and low π-acidity of the ligand would be expected to favor transfer of electrons from the ligand to the metal. At the

same time, decreasing the ease of reduction of the metal would disfavor this ligand to metal charge transfer. Other factors such as metal ion size and charge must also be considered. In this work a number of these factors will be examined in regard to the stabilization of complexes between sulfur donor ligands and the early transition metals. Discussions will be limited to the ions M(+4) for Ti, Zr and Hf; and M(+5) for Nb and Ta, which are the dominant oxidation states of these metals. Complexes of these ions with sulfur containing ligands have been well reviewed,[2-4] but a brief review of the present state of knowlege in this area will be presented here.

The greatest number of complexes involving the early transition metals and sulfur donors are adducts between thioethers and metal halides. Due to the ready availability of titanium halides, the greatest number of investigations are with this metal. For example, compounds of the type $TiX_4 \cdot 2L$ have been prepared for $L=R_2S$ (where R=Me, Et, Pr^n, Bu),[5-7] $L=(CH_2)_nS$ (where n=3,4,5),[5,8] $L=[RS(CH_2)_2SR]_4$ (where R=Me, Et, and Ph),[5,6,9] and L=1,4-thioxan (C_4H_8OS),[11] where in all cases X=Cl

and Br. In contrast to this, Compounds of the type $MX_4 \cdot 2L$ are somewhat more limited for Zr and Hf. Zirconium halides ZrX_4 (X=Cl or Br) form adducts $ZrX_4 \cdot 2L$ with tetrahydrothiophene and $CH_3SCH_2CH_2SCH_3$ (the latter has only been added to $ZrCl_4$).[12] The ligands 1,4-thioxan and $(CH_3)_2S$ form $ZrCl_4 \cdot L$ adducts.[13,14] In the cases of Ta and Nb, the predominance of six coordination results in adducts of the type $MX_5 \cdot L$ for $L=(CH_2)_nS$ (for n=4,5 and X=Cl or Br),[15] $L=R_2S$ (where R=Me, Et, Pr^n, and X=Cl or F),[16,17] and L=1,4-thioxan.

More recently it was found that titanium tetrachloride will also form adducts with mercaptans.[18] Compounds of the type $TiCl_4 \cdot 2RSH$ were formed (where R=Et, Pr^n, Bu^n, or Ph), while dithiols formed 1 to 1 adducts. The monothiol adducts were reported to be thermally stable, while the dithiol adducts evolved two equivalents of HCl on heating to yield dichlorodithiolates, such as $TiCl_2(SCH_2CH_2S)$.

The second important class of compounds between sulfur containing ligands and the early transition metals is the dithiocarbamates. This is the largest group of compounds where sulfur is the only atom bonded to the transition metal ion. Bradley and Gitlitz have found a convenient way of preparing these compounds

through CS_2 insertion into the appropriate metal amides,[19] as illustrated below:

$$M(NR_2)_4 + CS_2 \longrightarrow M(S_2CNR_2)_4 \quad (1)$$

(for M=Ti or Zr and R=Me, Et, and Pr^n).

This prodecure produced $Ta(S_2CNMe_2)_5$ from $Ta(NMe_2)_5$, but the corresponding Nb compound was reduced to $Nb(S_2CNMe_2)_4$. Alternatively, reaction of the sodium salt of a dithiocarbamate with a metal halide produces mixed halo-dithiocarbamato complexes, where the relative amounts of each ligand depend upon the amount of sodium dialkyldithiocarbamate used.[20-23]

$$MCl_5 + xNa\ S_2CNR_2 \longrightarrow MCl_{5-x}(S_2CNR_2)_x \quad (2)$$

Structural work with dithiocarbamates has shown $Ti(S_2CNEt_2)_4$ to be a D_{2d} dodecahedron,[24] and the mixed complex $TiCl(S_2CNEt_2)_3$ was found to be a slightly distorted pentagonal bipyramid.[25]

A third group of compounds is the mercaptides, which are relatively few in number. In the reaction between thiols and titanium tetrachloride, complete displacement of the chlorides cannot be achieved. However, reaction between metal amides and alkylthiols produces compounds of the type $Ti(SR)_4(RNH_2)_x(RSH)_y$ (where R is Me, Et, Pr^i and x and y are highly variable).[26] These compounds were thought to be polymeric and were generally difficult to

work with. Complete displacement of chloride ions from the metal chloride has been achieved by reacting $Al(SC_6H_5)_3 \cdot Et_2O$ with MCl_x in Et_2O or C_6H_6 (where M=Ti and Zr, X=4, or M=Nb and Ta, x=5). The resulting complexes had the formula $M(SC_6H_5)_x$.[27] Generally these mercaptides were sensitive to atmospheric moisture and in some cases were also thermally unstable.[26]

The final group, complexes of unsaturated 1,2-dithiols, will form a large part of this work, so it is appropriate to more carefully review some of the past work on these complexes before beginning to describe recent efforts in this area. As will be seen later, these complexes are characterized by a high degree of covalent bonding, the importance of which, in the stabilization of sulfur complexes of the early transition metals, will become evident as the properties of several new compounds are examined.

The past work in the area of transition metal complexes of 1,2-dithiolenes has been well reviewed,[28-34] thus only the conclusions drawn from previous work will be mentioned here for comparison with the results of this work.

Intense investigation into the chemistry of 1,2-dithiolene complexes began about 1960, when several

groups of researchers simultaneously discovered convenient routes for preparing the compounds.[35-39] Prior to that time, intermittant studies had centered around the analytical uses of dithiols while investigations into the properties of these complexes were largely neglected.[40-41]

The first new aspect of their chemistry was the observation that the complexes may be readily oxidized or reduced; and by means of polarography, the same complexes could sometimes be observed with a variety of different overall charges. In some cases, the oxidized or reduced forms of complexes could even be isolated as pure compounds. The classification of ligand systems by G. N. Schrauzer as being "even" or "odd", according to the number of atomic orbitals within the ligand system available for π-bonding, is useful in understanding the unique electrochemical behaviour of 1,2-dithiolenes.[36] The presence of a weakly antibonding level in the "even" systems permits them to exist as the neutral ligand, monoanion or dianion, Figure 1. The "odd" systems, on the other hand, favour the monoanion alone. In valence-bond terms, 1,2-dithiolenes and other "even" ligands may exist as neutral ligands or dianions by invoking the dithioketone or dithiolate electronic structures.

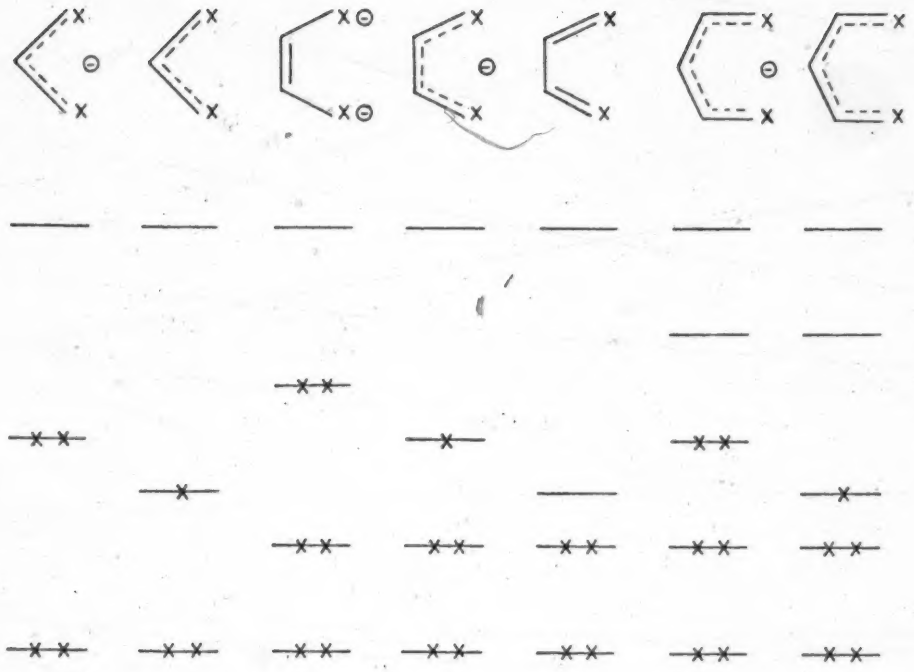
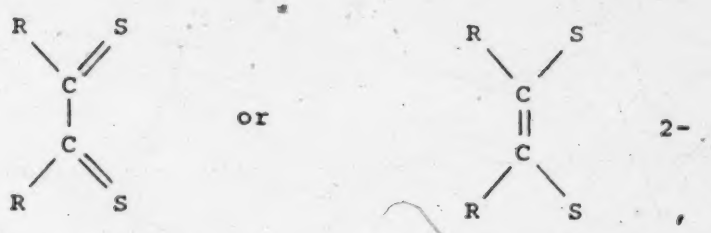
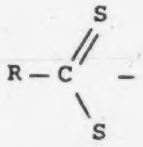


Figure 1: Qualitative Molecular Orbitals for "Even" and "Odd" Ligands.[a]

[a]After G. N. Schrauzer, ref. 31.



while the "odd" ligands again provide only one suitable electronic structure, the monoanion:



It may be easily seen that the "even" ligand systems cause some difficulty when assigning a formal oxidation state to the central metal. For example, in one extreme the ligands in $Mo(S_2C_2H_2)_3$ may be considered to be dianions and the Mo +6, or in the other extreme the lilands and Mo atom may all be thought of as neutral. The important question is the relative participation of metal and ligand orbitals in the occupied molecular orbitals of the complex. As in all highly covalent compounds, oxidation states must be approached from this standpoint. A further similar question is whether the ligands or the metal undergo oxidation or reduction during electron transfer reactions. Again, the nature of the molecular orbitals being populated or depopulated must be considered. The existence of compounds such

as: $V(S_2C_2Ph_2)_3$, where considering the ligands as dianions would result in the unlikely V^{6+}, demonstrates that the dithiolene ligands must play a major role in the redox reactions of their complexes.

The second feature of 1,2-dithiolene complexes which resulted in intense study in this area of chemistry was their stabilization of nearly perfect square planar geometry in all of the 2 to 1 complexes, except possibly those of Zn and Cd,[29] and the stabilization of trigonal prismatic geometry for some of the 3 to 1 complexes. Prior to this study, three tris dithiolene complexes: $V(S_2C_2Ph_2)_3$, $Mo(S_2C_2H_2)_3$ and $Re(S_2C_2Ph_2)_3$, had been established by x-ray crystallography to have trigonal prismatic geometry.[32] While the ligands in the Re and V complexes were planar, the ligands in the Mo complex were bent by 18^o about the intraligand S-S axis. A similar bend was noted in some of the organometallic complexes of the type $(\eta^5\text{-}C_5H_5)_2M(S_2C_2R_2)$ (where R=H or CN or $S_2C_2R_2$ is benzenedithiol, and M=Ti or Zr).[42-44] The benzene-1,2-dithiol and ethylene-1,2-dithiol complexes with Ti were found by x-ray crystallography to have a bend of 46^o around the S-S axis.[45,46] The only two tris dithiolene complexes known for the early transition

metals $Ti[S_2C_2(CN)_2]_3^{2-}$ and $Ti(S_2C_6Cl_4)_3^{2-}$ have not been structurally characterized.[47,48]

Clearly, the unusual structural features of 1,2-dithiolene complexes must arise for the same reasons that their electrochemical behaviour is unique. Two features of their bonding have been suggested to explain the observed geometries; they are: interligand S-S bonding, and highly delocalized bonding between the metal and ligand system.[31] The postulate of interligand S-S bonds arose mainly from the similarity of interligand S-S distances in both the 2 to 1 and 3 to 1 complexes.[32] Typically, these contacts were found to be ~3.1Å. For instance, in the series: $V(S_2C_2Ph_2)_3$, $Mo(S_2C_2H_2)_3$ and $Re(S_2C_2Ph_2)_3$, the inter and intraligand S-S distances were approximately constant despite the varying size of the central metal.[49] The importance of delocalized metal to ligand bonds manifested itself in other respects, such as charge transfer bands in the visible region of the spectrum.

In an effort to explain the highly unexpected occurence of trigonal prismatic geometry in some of the 3 to 1 complexes, G. N. Schrauzer[50] and H. B. Gray[51] separately reported the results of molecular orbital

Schrauzer and Mayweg

Gray, *et. al.*

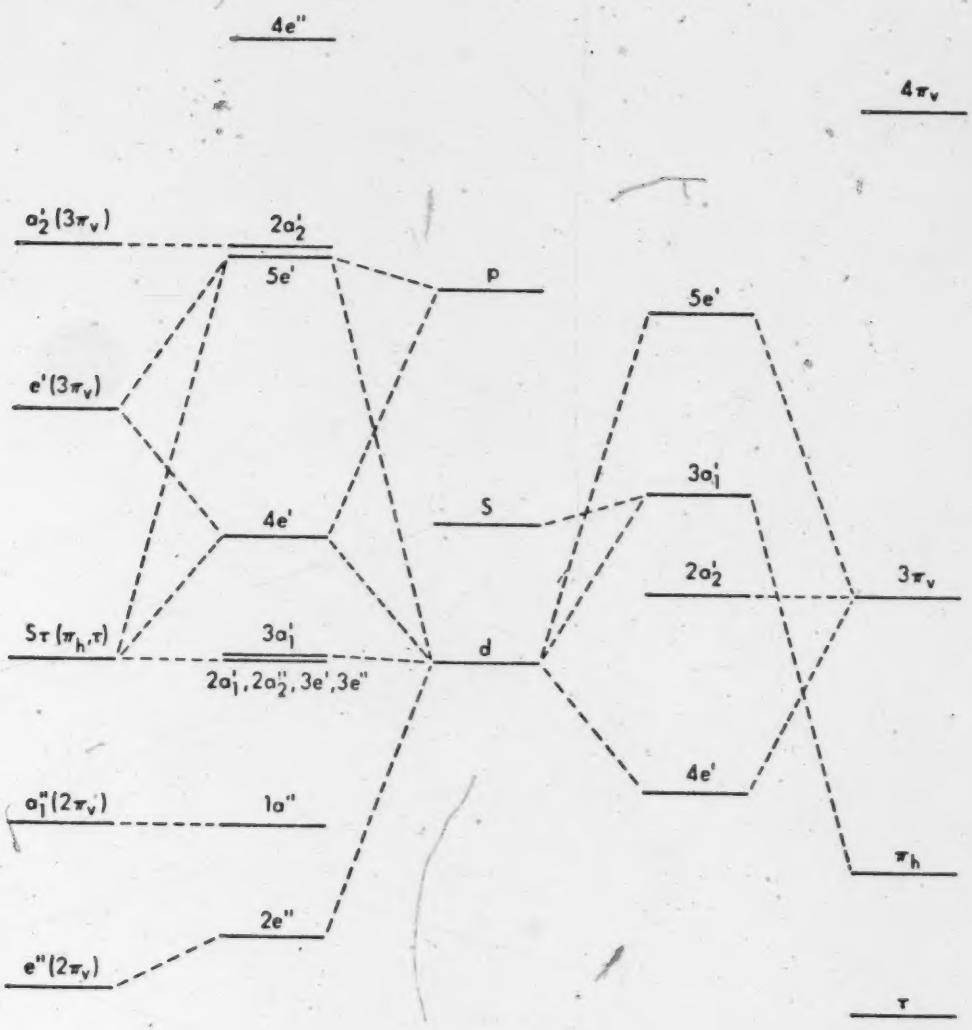


Figure 2: Comparison of the Molecular Orbital Schemes of Gray and Schrauzer.

calculations for the ethylenedithiol and stilbenedithiol systems respectively, Figure 2. In both schemes, the formation of a 4e' molecular orbital which is highly delocalized over the metal and the ligand system has been suggested as a major factor in the stabilization of trigonal prismatic geometry. Both schemes also take into account the formation of interligand S-S bonds, but Gray's scheme also suggests the formation of a bond between orbitals on the sulfur atoms, and in the plane of the ligand, and the dz^2 orbital of the central metal atom. The formation of this bond seems to be the major difference between the two schemes although there is also some difference between the relative ordering of metal and ligand orbitals. Unfortunately the authors do not provide the mixing coefficients and Gray does not supply an energy scale so that it is difficult to correlate results with the schemes. The principle levels of interest for this discussion are shown in Figure 2. In the scheme described by Schrauzer, the 4e' is the highest occupied orbital and is composed of 41% ligand π, 17% sulfur sp^2, 25% metal d and 17% metal p character. The 5e' is similar to the 4e', but with substantially more metal character, while the $2a_2'$ is a pure ligand π -orbital. In the Gray scheme, the only information given is that the highest occupied orbital, the $2a_2'$, is a ligand π_v orbital, while the 4e' and

5e' have considerable metal and ligand character.

A qualitative molecular orbital calculation to compare the relative stabilities of the trigonal prism and octahedron has also been made.[52] It was concluded that strong covalent bonding between the ligands and the metal should favor the trigonal prism just on the basis of σ-bonding, while π-bonding was considered to be of minor importance. Unfortunately these authors did not present detailed calculations of any of the dithiolene complexes. However, the qualitative ordering of molecular orbitals was very similar to that given by Gray.

While structural investigations on neutral tris dithiolene complexes showed them to be trigonal prismatic, anionic complexes studied before this work were shown to be highly distorted toward octahedral geometry.[32,53] It has been reasoned that increasing the charge on the complex will increase interligand repulsive forces and thus favor octahedral geometry. In keeping with this explanation, the interligand S-S contacts in anionic complexes were found to be considerably larger than in the neutral trigonal prismatic complexes.[32] In addition, the molecular orbital scheme of Gray demands that these additional electrons go into an orbital which is largely metal dz^2 in character and hence antibonding with respect to the metal-sulfur bond.

Furthermore, in complexes such as $Fe[S_2C_2(CN)_2]_3^{3-}$, which has been found to be octahedral and is formally a low spin d^5 system, ligand field stabilization energy must certainly play an important role in favoring octahedral geometry.[54]

Apart from x-ray crystallography, visible-UV spectra have been the most important structural tool available for studying transition metal dithiolene complexes. Particularly, it has been considered that an intense transition (with $\log \varepsilon \sim 4.0\text{-}5.0$) at lower energy than about 20,000 cm^{-1}, indicates trigonal prismatic geometry, especially for the neutral or singly charged complexes.[50,51] The assignment of this transition, based upon the previously mentioned molecular orbital schemes, appears to be considerably different for the two schemes. Gray has stated that the transition is essentially ligand to metal ($2a_2' \rightarrow 5e'$) charge transfer, while Schrauzer states that it is essentially ligand π to π^*($4e'$ $5e'$). In addition to a difference in the metal dependence, the degeneracies of the transitions are different which in theory should allow one to distinguish between the two assignments. In constructing Figure 2, because the Gray scheme had no energy scale, it was necessary to assume that the same

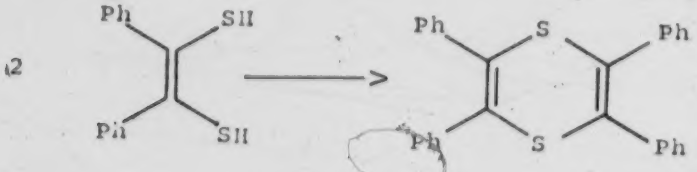
metal was being used for both schemes and that the separations $2a_2'$ to 5e', in the Gray scheme, and 4e' to 5e' in the Schrauzer scheme, were of the same magnitude.

A further word in regard to the electrochemical behaviour of the 3 to 1 complexes is warranted; namely that it is somewhat more restricted than for the 2 to 1 complexes. Particularly it should be noted that only two of the former complexes, $Re(S_2C_6H_3CH_3)_3$ and $Re(S_2C_2Ph_2)_3$, have been observed to undergo oxidation to positively charged compounds; these two complexes are also the only complexes formally having the d^1 configuration, while all others are d^0.

Having reviewed the properties of 1,2-dithiolene complexes, it will be useful to consider briefly the methods which have been used to prepare these compounds. Since the subject of this work will be 3 to 1 complexes, the synthesis of 2 to 1 complexes will not be mentioned although it may be said to be very similar to that of 3 to 1 complexes. Probably the majority of synthetic routes known to date use anhydrous metal chlorides as starting materials. For example, toluene-3,4-dithiol and benzene-1,2-dithiol react with $MoCl_5$ or WCl_6 to yield neutral 3 to 1 complexes as in (3).[51]

$$WCl_6 + 3(HS)_2C_6H_4 \longrightarrow W(S_2C_6H_4)_3 + 6HCl \qquad (3)$$

Reaction 3 is unfortunately restricted since many 1,2-dithiols are not stable. For example stilbenedithiol is believed to decompose according to (4).[55]



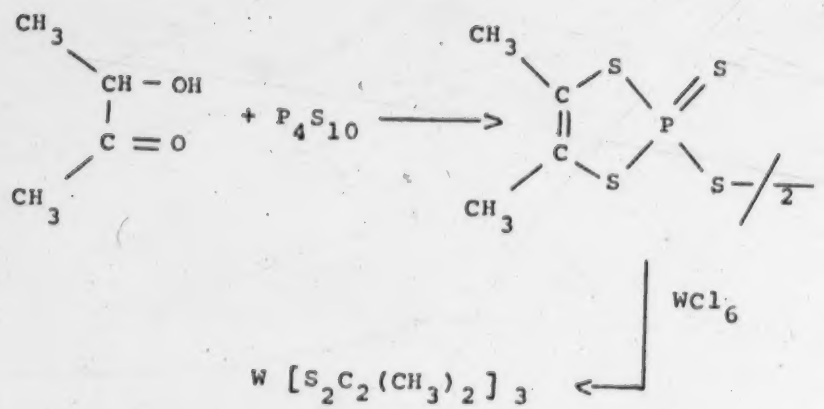
(4)

This difficulty has been overcome for some of the ligands which are stable as disodium salts and provide the alternate route illustrated by (5) and (6).

$TiCl_3$,
$Na_3Co(CO_3)_3 \cdot 3H_2O$,
$CrCl_3 \cdot 6H_2O$,
$FeCl_3 \cdot 6H_2O$, $+ Na_2S_2C_2(CN)_2 \rightarrow M[S_2C_2(CN)_2]_3^{2-}$ (5)
$Mn(O_2CCH_3)_3 \cdot H_2O$,
$ReCl_5$, WCl_6 or $MoCl_5$

Na_2MoO_4, Na_2WO_4,
Re_2O_7, $VO(acac)_2$ $+ Na_2S_2C_2H_2 \rightarrow M(S_2C_2H_2)_3$ (6)

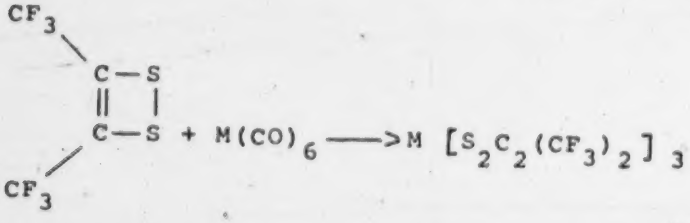
An alternate route, developed by Schrauzer, employs phosphorus esters of the ligand, prepared and used as in (7).[56]



(7)

Metal carbonyls are also suitable starting materials according to (8) and (9).[56-58]

$$M(CO)_6 + PhC{\equiv}CPH + S \longrightarrow M(S_2C_2Ph_2)_3 \quad M=Cr, Mo, W \qquad (8)$$



M=Cr, Mo, W (9)

The methods used in preparing the previously mentioned early transition metal complexes were (5) for $S_2C_2(CN)_2$,[47] and a variation of the same procedure in which the dipotassium salt of 3, 4, 5, 6-tetrachlorobenzenedithiol was prepared in ethanol and reacted with $TiCl_4$ without isolation.[48]

CHAPTER 2: THE SYNTHESIS OF TRIS-DITHIOLENE COMPLEXES

In chapter 1 a number of synthetic methods were presented for preparing 1,2-dithiolene complexes. The application of these routes to the early transition metals was an obvious extension of previous research. However in this work a slight modification was made in that 4 to 1 ligand to metal mole ratios were employed. It was felt that the predominance of eight coordination among the early transition metals[59] might explain the apparent failure of other researchers to synthesize dithiolene complexes with these metals. Several of the procedures outlined in chapter 1 were attempted. For example, $ZrCl_4$ was reacted with toluene-3,4-dithiol in carbon tetrachloride, diethylether and tetrahydrofuran in separate trials. No reaction was apparent in tetrahydrofuran, while from diethylether an adduct between the solvent and $ZrCl_4$ was isolated. From CCl_4, a dark red oil was obtained which in retrospect may have been $Zr(S_2C_6H_3CH_3)_3H_2$, but was not characterizable due to its polymeric nature.

In another attempt, $ZrCl_4$ was added to the sodium salt of toluene-3,4-dithiol prepared in anhydrous ethanol. An IR of the light-yellow product had an intense OH stretch indicating that hydrolysis had occurred.

Reactions according to equations 4 and 6 were also tried in a variety of solvents with $ZrCl_4$ without success. Finally it was concluded that a more orderly approach should be taken. One may observe that several of the reactions previously outlined are not straightforward in terms of stoichiometry and oxidation or reduction. Ideally, it was thought, eight coordinate complexes could be prepared by the reaction between a dithiol and a metal complex of the type $M(B)_4$ (where B is a diprotic base) in a 4 to 1 ratio. Such a base seemed to be NR_2^-, which has the capability of reacting all the way to $H_2NR_2^+$. The investigations of Bradley and Hammersly[26] into the reactions of $M(NR_2)_4$ (where M is Ti, Zr, or Hf) with alkylthiols, discussed in chapter 1, showed that there was hope for the desired reaction if one paid attention to stoichiometry, and if the dithiol was sufficiently acidic. Since no measurement of the acidity of toluene-3,4-dithiol could be found, the next best alternative was to try the reaction. It was soon found that reaction of toluene-3,4-dithiol with $Ti[N(C_2H_5)_2]_4$ in toluene produced a black compound which has been tentatively formulated as $[(C_2H_5)_2NH_2]_2$ Ti $(S_2C_6H_3CH_3)_3$,as will soon be described. The realization that six-coordinate compounds

could be made from the metal amides initiated the work which will form the bulk of this thesis.

EXPERIMENTAL

Throughout this work operations were performed under nitrogen atmosphere in Schlenk type apparatus. The basic procedures used have been adequately described by a number of authors.[60-62] Commercial nitrogen of 99.99% purity or better was passed through a heated column of BASF catalyst #R3-11 to remove oxygen and then through a column of Mallinkrodt Aquasorb, which is P_2O_5 on an inert base, to remove water. Tetrahydrofuran, toluene and ether were purified by distillation from flasks containing Na, K or Na/K alloy. Acetonitrile and CH_2Cl_2 were distilled from P_2O_5, but CH_2Cl_2 was first washed with concentrated H_2SO_4 and water and dried over $CaSO_4$. Tetralkylammonium and tetraphenylarsonium salts were reagent chemicals dried for about 15 hours at 100° C. and 0.1 mm Hg prior to use. Hexanes solutions of n-butyllithium were purchased from Foote Chemical Co., while toluene-3,4-dithiol was obtained from Eastman Kodak or Matheson, Coleman and Bell.

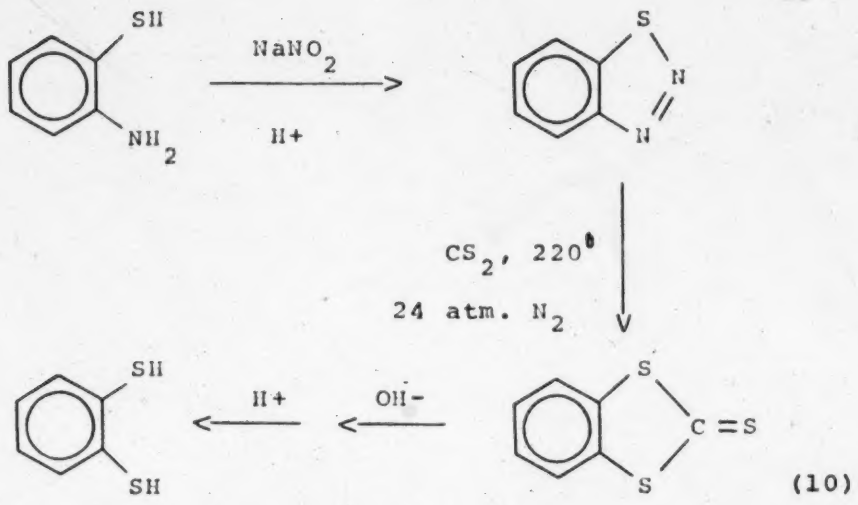
Metal amides were prepared by previously published procedures[63-66] with the following

cautions. Although commercially available $NbCl_5$ was found to be suitable in the synthesis of metal amides, $TaCl_5$ was instead prepared from Ta metal and Cl_2 gas by the method of Ellis[67] or some other suitable procedure.[68] Also, the air sensitive Nb and Ta amides were difficult to transfer from a sublimation probe to a Schlenk tube. A special apparatus, which is essentially a Claisen condenser with a nitrogen inlet built into the side, at the top, was devised for this sublimation. The condenser-like apparatus was fitted to a flask containing the crude product and once sublimation was over, the flask was replaced by a Schlenk tube and the product was scraped down into the tube under N_2.

Sodium cyclopentadienide was prepared in the following way: in a 1ℓ 3-neck flask fitted with an air condenser, N_2 inlet, dropping funnel and high speed mechanical stirrer with a large paddle adjusted to reach the bottom of the flask, freshly cut and cleaned sodium metal, 23 g, was added to 70 ml of dry Toluene. The mixture was heated until the metal was molten, then vigorous stirring was commenced. After about 5 minutes, the heating was removed and the stirring

was stopped. The Na sand was allowed to cool to room temperature undisturbed and the toluene was removed by syringe and was replaced by 600 ml of dry THF. Next, 90 ml of freshly distilled cyclopentadiene was added dropwise with stirring over a period of 3.5 hours, with the resulting evolution of hydrogen and heat. Finally, 5 ml of cyclopentadiene was again added and the mixture was stirred an additional 12 hours resulting in a colorless solution. The flask was then fitted with a N_2 inlet equipped with a vacuum stopcock and the dropping funnel, condenser and mechanical stirrer were quickly removed while a magnetic stirring bar was added. The solvent was removed under vacuum and the resulting white solid thoroughly dried. Benzene-1,2-dithiol was prepared according to the following modification of the method of Hunig and Fleckenstein,[69] equation 10.

The 1,2,3-benzothiadiazole was prepared as follows: in a 1ℓ 3-neck flask fitted with a dropping funnel, thermometer, and mechanical stirrer, 100ml of o-aminothiophenol[70] was dissolved in 400 ml of glacial acetic acid and 40 ml of water. This mixture was cooled in an ice-methanol bath and kept at 0-5° C throughout the addition of a



(10)

solution of 65 g of $NaNO_2$ in 200 ml of water. Addition was stopped as soon as a persistant brown color was observed. The mixture was then stirred overnight followed by extraction with three 200 ml portions of CH_2Cl_2. The extract was washed with an aqueous 5% $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed with a water aspirator and the product was distilled at 56° C and 0.1 mm Hg to yield 103 g (43%) of 1,2,3-benzothiadiazole as a low melting solid. From this point on, the synthesis follows basically the procedure of Hunig and Fleckenstein, given here for the reader's convenience.

The 1,2,3-benzenethiadiazole, 103 g, was dissolved in 850 ml of CS_2 and was transferred to a 2ℓ autoclave. The autoclave was sealed, flushed with N_2, and finally pressurized to 350 p.s.i. with N_2. The system was heated to 440° F., causing the pressure to rise to 750 p.s.i., and stirring was continued at this temperature for 5 hours while the pressure rose to 1000 p.s.i.

The system was then allowed to cool to room temperature overnight, the autoclave was depressurized, and the mixture of solution and solid removed. The solvent was stripped off the mixture leaving 86 g of crude product, 79% yield of benzo-1,3-dithia-2-thione.

In a 1ℓ 3-neck flask fitted with a condenser, 90 g of KOH was added to 700 ml of ethyleneglycolmonomethylether and the solution was degassed by passing dinitrogen through it. Next, 55 g of benzo-1,3-dithia-2-thione was added and the resulting dark brown solution was refluxed for 3 hours. The solvent was removed by steam distillation; the endpoint being signaled by foaming of the reaction mixture. The reaction mixture was carefully acidified with 125 ml of concentrated HCl (COS evolution) and the product was steam distilled over 4.5 hours. The distillate was extracted with CH_2Cl_2 and the extract was dried over $MgSO_4$. The solvent was removed on a rotavap yielding 30 g, 70%, of the crude product, which was further purified by vacuum distillation to give 26 g of a colorless liquid, 61% yield.

Preparation of the Complexes:

Method 1, Direct Reaction

$[(C_2H_5)_2NH_2]_2 \quad Ti(S_2C_6H_3CH_3)_3$

Toluene-3,4-dithiol 0.762 g (0.00486 mole), was dissolved in 25 ml of dry toluene in a 3-neck flask fitted with a nitrogen inlet, dropping funnel and magnetic stirrer. A solution of $Ti[N(C_2H_5)_2]_4$, 0.407 g (0.00121 mole) was added dropwise from the dropping funnel resulting in the formation of a dark red-brown solution and a black solid. The reaction mixture was stirred for 24 hours with no apparent change and then refluxed for 2 hours which caused more precipitate to form. The black solid was collected by filtration to give 0.765 g, 96% based on Ti. The product may be recrystallized from mixtures of acetone and light petroleum ether in about 60% yield; mp 261-263° uncorrected.

Anal. Calcd: C, 52.86; H, 6.43; N, 4.25; Ti, 7.27. Found: C, 53.07; H, 6.48; N, 4.11; Ti, 7.24.

This compound could also be obtained from reactions of 3 moles of toluene-3,4-dithiol with 1 mole of the amide, as identified by the IR, ^{1}H-NMR and melting point evidence.

Method 2, Use of n-Butyllithium

$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_3CH_3)_3$

A solution prepared by adding 2.5 ml of a 1.67N hexanes solution of n-butyllithium to 10 ml of THF, was added dropwise to 0.646 g (0.00415 mole) of toluene-3,4-dithiol in 25 ml of THF. After 1/2 hour, 16 ml of a solution of 0.428 g (0.00127 mole) of $Ti[N(C_2H_5)_2]_4$ in 20 ml of THF was added dropwise to the reaction mixture. (Only the amount of the Ti solution required by the stoichiometry of the reaction was added, the rest was discarded.) The resulting mixture was stirred overnight and then 1.099 g of $(C_2H_5)_4NI$ was added directly. The resulting mixture was stirred for several days and then the solvent was removed under vacuum and was replaced by 25 ml of methanol. After stirring for 1 hour, the reaction mixture was allowed to settle for 3 hours and the resulting black, microcrystalline solid was collected by filtration in the open. After drying under vacuum the yield was 0.257 g (33%); mp 229-330° uncorrected.

Anal, Calcd: C, 57.63; H, 7.58; N, 3.64; S, 24.95. Found: C, 57.18, 57.43; H, 7.50, 7.39; N, 4.11,4.05; S, 25.19, 25.62.

$[(C_4H_9)_4N]$ $Nb(S_2C_6H_3CH_3)_3$

The procedure used here was essentially the same as for Ti except that methanol was not used for the exchange. Instead 10 ml of CH_2Cl_2 was added to dissolve the crude product then 190 ml of ether was added and, after brief stirring, a violet solid was filtered off. The product was recrystallized by dissolving it in 100 ml of CH_2Cl_2 and adding 100 ml of ether. After standing for four days, violet crystals were collected. Two further crystallizations gave violet hexagons in 13% yield, decomp. 160°.

Anal. Calcd: C, 55.68; H, 6.82; N, 1.75; S, 24.10; Nb, 11.64. Found: C, 55.92, 55.82; H, 6.58, 6.57; N, 1.79, 1.72; S. 24.11, 24.10; Nb, 11.50, 11.29.

Method 3, Use of Sodium cyclopentadienide

$[(C_2H_5)_4N]_2$ $Hf(S_2C_6H_3CH_3)_3$

Sodium cyclopentadienide, 0.508 g (0.00578 mole), in 20 ml of THF was added to 1.268 g (0.00815 mole) of toluene-3,4-dithiol in 50 ml of THF. Next, 1.23 g (0.00264 mole) of $Hf[N(C_2H_5)_2]_4$ in 20 ml of THF was added dropwise to the reaction mixture and the resulting orange solution was stirred overnight. Tetraethylammonium bromide, 1.23 g (0.00578 mole),

was added to the reaction mixture and after about 1 hour of stirring the solvent was removed under vacuum and the residue was thoroughly dried. The residue was stirred with 150 ml of CH_3CN for 1/2 hour and then filtered to remove NaBr. By concentrating the filtrate under vacuum and cooling it in a freezer, 1.234 g (55%) of an orange solid was obtained, mp 232-233° uncorrected.

Anal. Calcd: C, 49.15; H, 6.47; N, 3.10; S, 21.28. Found: C, 48.58, 48.48; H, 6.36, 6.54; N, 3.00,3.06; S, 21.41, 21.15.

Using similar synthetic procedures, the following compounds were also obtained.

$[(C_2H_5)_4N]_2\ Zr(S_2C_6H_3CH_3)_3$

Red crystals, mp 229-230° uncorrected, 46% yield. Anal. Calcd: C, 54.56; H, 7.18; N, 3.44; S, 23.62. Found: C, 54.23, 54.15; H, 7.44, 7.47; N, 3.69, 3.70; S, 22.62, 22.87.

$[(C_2H_5)_4N]_2\ Zr(S_2C_6H_4)_3$

Red crystals, mp 227° uncorrected, 60% yield. Anal. Calcd: C, 52.87; H, 6.78; N, 3.63; S, 24.91. Found: C, 53.59, 53.12; H, 6.95, 7.17; N, 3.68; S, 25.27, 25.45.

$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_4)_3$

Black, crystalline solid mp 224-225° C uncorrected,

80% yield. Anal. Calcd: C. 56.01; H, 7.19; N, 3.84; S, 26.39. Found: C, 55.78; H, 7.00; N, 3.27; S, 25.84.

$[(C_2H_5)_4N]$ $Ta(S_2C_6H_3CH_3)_3$

Dark brown crystals, decomp. 206°, 27% yield. Anal. Calcd: C, 45.00; H, 4.95; N, 1.81; S, 24.86. Found: C, 44.11, 44.18; H, 4.82, 5.03; N, 1.57, 1.92; S. 23.87, 23.46.

$[(C_6H_5)_4As]$ $Nb(S_2C_6H_4)_3$

Instead of treating the residue with CH_3CN, it was transferred to a continuous extractor and extracted with 100 ml of CH_2Cl_2. Concentrating and cooling the extract gave violet crystals in 38% yield, decomp. 214° uncorrected. Anal. Calcd: C, 56.25; H, 3.60; S, 21.45. Found: C, 56.36, 56.17; H, 3.86, 3.80; S, 21.46, 21.19.

$[(C_6H_5)_4As]$ $Ta(S_2C_6H_4)_3$

Instead of treating the residue with CH_3CN, it was dissolved in CH_2Cl_2 and filtered to remove NaCl. As before a dark-brown solid was obtained, decomp. 220°. Yield: 47%. Anal. Calcd: C, 51.22; H, 3.28; S, 19.53. Found C, 50.78, 50.69; H, 3.22, 3.60; S, 20.00, 19.44

$[(CH_3)_4N]_2Zr(S_2C_6H_4)_3$

Crystals of this compound were prepared for study by x-ray crystallography in the following manner: Sodium cyclopentadienide, 0.190 g (0.00216 mole), in 20 ml of THF was added to 0.00324 mole of benzene-1,2-dithiol in 20 ml of THF. To this mixture, 0.430 g (0.00113 mole) of tetrakisdiethylamidozirconium was added in 20 ml of THF. After stirring overnight, 0.231 g (0.00211 mole) of dry tetramethylammonium chloride was added. The solvent was then removed under vacuum and replaced by 50 ml of CH_3CN. After stirring for 24 hours a brown solid and a brownish-yellow solution were obtained. The brown solid was filtered off and dried under vacuum, and was finally dissolved in 50 ml of CH_3CN with heating. The orange solution was filtered hot and 30 ml of CH_3CN was added to retard crystallization. After cooling to room temperature, the solution was cooled overnight in a refrigerator to yield a small amount of red crystals.

The following compounds were also prepared for purposes of comparison:

$[(C_6H_5)_4As]\ Sb(S_2C_6H_4)_3$

This compound was prepared by the method of Gagliardi and Durst.[71] Anal. Calcd: C, 54.49; H, 3.48;

S, 20.78. Found: C, 53.82; H, 3.62; S, 20.40.

$Mo(S_2C_6H_4)_3$ and $W(S_2C_6H_3CH_3)_3$

These complexes were prepared by the method of Gray, *et. al.* and were characterized by physical methods.

Physical Measurements:

Conductivity measurements were made at 10^{-3}M in CH_3CN using a cell designed for work under inert atmosphere, Figure 3, and a Philips PR9500 conductivity bridge. Molecular weight measurements were made at 10^{-3}M in CH_3CN using a Hewlett-Packard 301 A vapor phase osmometer calibrated with benzil. Infrared spectra were recorded in the region of 4000 to 250 cm^{-1} as mineral oil mulls and very thin KBr pellets on a Perkin-Elmer 467 infrared spectrophotometer. Visible and ultraviolet spectra were recorded from 10,000 to 40,000 cm^{-1} on a Cary 14 at 10^{-4}M in CH_3CN using various path lengths. ^{1}H-NMR spectra were recorded on a Varian Associates A60 or HA-100 or Perkin-Elmer R32, while ^{13}C spectra were recorded on a Brüker HFX-10. Polarographic measurements were made using conditions and apparatus similar to that described in detail by Holm, *et. al.* .[72] Measurements in CH_3CN were made at 10^{-3} M with 0.1 M $(n\text{-}C_3H_7)_4NClO_4$ as supporting electrolyte. The apparatus used for

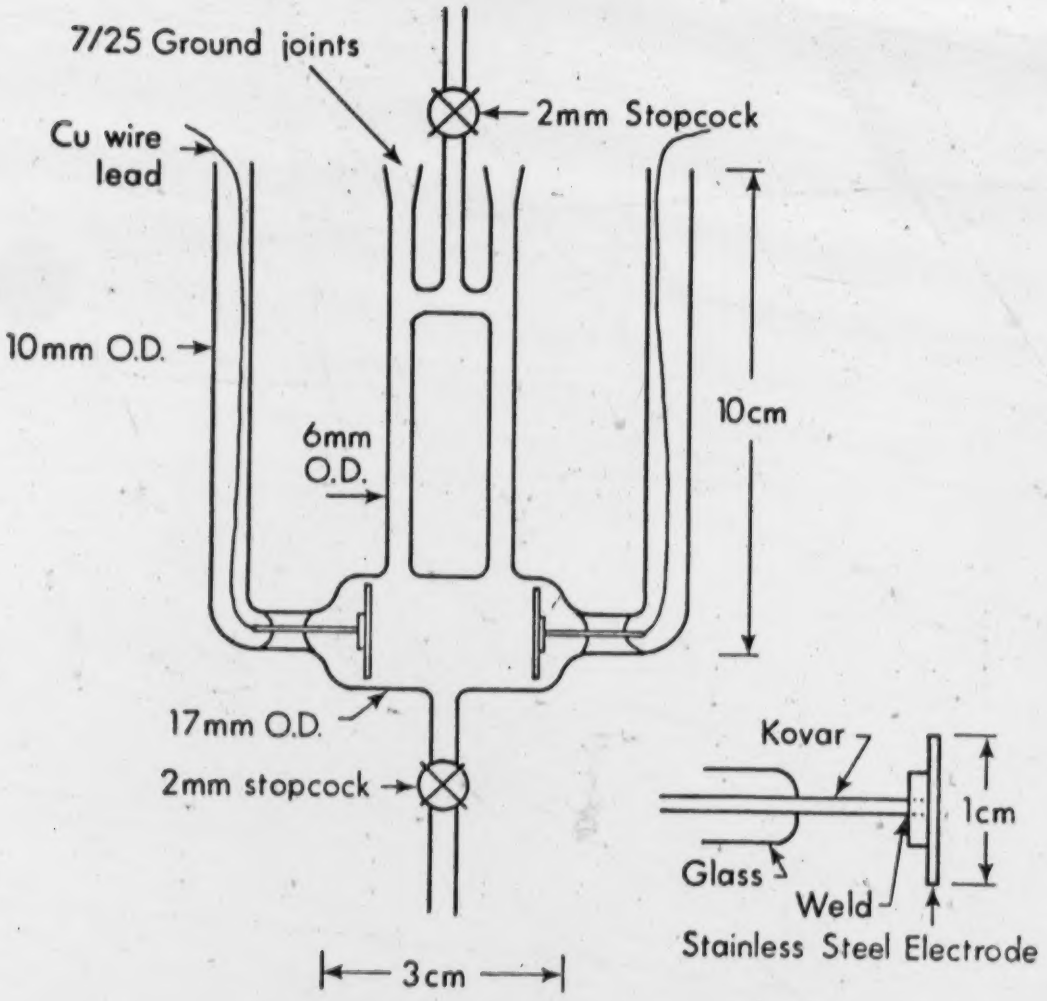


Figure 3: Conductivity Cell for Work Under Inert Atmosphere.

CH_3CN was the same as that used for CH_2Cl_2 except that the bridge was composed of silica gel impregnated with 0.1 M $(n\text{-}C_3H_7)_4NClO_4$ in CH_3CN, and the reference electrode was Ag | 0.1M $AgClO_4$, 0.1 M $(n\text{-}C_3H_7)_4NClO_4$. The indicator electrode was a platinum microelectrode[73] rotated at a constant speed of 600 r.p.m. The electrode was pretreated with concentrated HNO_3 for several minutes followed by water washing and soaking in acidic ferrous ammonium sulfate for several minutes and again washing with water.[74] The electrode was prepolarized at potentials slightly more positive than the wave of interest before sweeping through it from positive to negative potentials. All polarographic measurements were made using a Metrohm Polarecord E261 with IR compensator E446.

Results and discussion:

As previously mentioned, the reaction between 4 moles of toluene-3,4-dithiol and 1 mole of tetrakisdiethylamidotitanium yielded a black solid tentatively formulated as $[(C_2H_5)_2NH_2]_2\ Ti(S_2C_6H_3CH_3)_3$ (I). This assignment is based upon the elemental analysis, IR (Table 1), and UV-visible spectra (Table 2). The IR spectrum conclusively shows the presence of the diethylammonium

Table 1: Infrared Spectra as KBr Pellets (cm^{-1})[a]

$[(C_2H_5)_2NH_2]_2\ Ti(S_2C_6H_3CH_3)_3$

3200-2600s br, 2460m sh, 2360w sh, 1610w sh 1575m, 1535sh, 1460m sh, 1449s, 1432m sh, 1389m, 1376m sh, 1325vw, 1306vw, 1270m, 1246m, 1204vw, 1156w, 1132m, 1107m, 1059m, 1037m, 867m, 803s, 773m, 712vw, 688m, 639w, 553m, 481m, 448s, 395m sh, 385s, 356s, 338m sh.

$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_3CH_3)_3$

2970m, 2910m sh, 2860m sh, 1570w, 1535vw, 1480s sh, 1447s, 1390s sh, 1365m sh, 1300vw, 1270m, 1257w sh, 1240m, 1205vw sh, 1181m sh, 1170m, 1130w, 1105m, 1078vw, 1041w, 1032w sh, 1000m, 868m, 798s, 708vw, 687m, 638w, 551m, 479m, 445m, 393w sh, 382m, 354s, 336w sh.

$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_4)_3$

3095vw sh, 3040w sh, 2980w, 2950w sh, 2550vw, 1544w, 1479s sh, 1453s sh, 1434s, 1417s sh, 1392s sh, 1369m sh, 1302w, 1272m, 1234m, 1181m sh, 1170m, 1150w sh, 1097m, 1046w sh, 1022m, 1002m sh, 928w, 851vw, 786m sh, 739s, 716w sh, 667m, 482m, 454w sh, 439w, 393m sh, 379s, 344s, 272m.

Table 1 continued

$[(C_2H_5)_4N]_2\ Zr(S_2C_6H_3CH_3)_3$

2979m, 2915sh, 2860sh, 1580w, 1480s sh, 1449s, 1392m sh, 1369m sh, 1302w, 1262m sh, 1245m, 1186m sh, 1175m, 1132w sh, 1109s, 1082vw sh, 1037m sh, 1005m, 869m, 801s, 710vw, 688w, 637w, 556w, 476w, 443m, 379w, 322s.

$[(C_2H_5)_4N]_2\ Zr(S_2C_6H_4)_3$

3090vw sh, 3035m sh, 2975m, 2940m sh, 2530vw, 1569w sh, 1544w, 1477s sh, 1453s sh, 1433s, 1416s sh, 1390s sh, 1370m sh, 1300w, 1265m, 1232m, 1180m sh, 1169m, 1150w sh, 1094s, 1040m sh, 659m, 479m, 440w sh, 370w, 320s.

$[(C_2H_5)_4N]_2Hf(S_2C_6H_3CH_3)_3$

2970m, 2940m sh, 2910m sh, 1575vw, 1475m sh, 1446s, 1388m sh, 1365w sh, 1300vw, 1255m, 1242m sh, 1179m sh, 1168m, 1125w sh, 1104s, 1030m, 1000m sh, 863m, 797s, 707vw, 685w, 634w, 551w, 473w, 440w, 378vw, 310s.

$[(C_4H_9)_4N]$ $Nb(S_2C_6H_3CH_3)_3$

3025w sh, 2955s, 2930s sh, 2868m sh, 1579m, 1478s, 1450s, 1380m, 1282w, 1243w, 1204w, 1150w, 1147w sh, 1105vw sh, 1090vw, 1030w, 872m, 802s, 750vw sh, 737vw, 710vw, 690w, 551w, 480vw, 442w, 398vw sh, 364m, 337w sh.

$[(C_6H_5)_4As]$ $Nb(S_2C_6H_4)_3$

3035w, 1570w, 1479m, 1434s, 1420s sh, 1334w, 1308w, 1280m, 1233m, 1181m, 1160m sh, 1154m, 1127w, 1096vw sh, 1078s, 1017w, 995m, 937w, 920w sh, 847w, 740s, 687s, 665m sh, 615vw, 477s, 465 s sh, 456m sh, 439m sh, 399m sh, 360s, 267m.

$[(C_2H_5)_4N]$ $Ta(S_2C_6H_3CH_3)_3$

3020w sh, 2960m sh, 2900m, 2860m sh, 1575w, 1479m sh, 1449s, 1392m sh, 1372m sh, 1300vw, 1275w sh, 1262w sh, 1248m, 1206vw, 1183w sh, 1171m, 1145vw sh, 1135vw, 1110m, 1033m, 869m, 811s, 785m sh, 708vw, 689m, 631m, 552m, 482w, 445m, 392w, 339s.

$[(C_6H_5)_4As]$ $Ta(S_2C_6H_4)_3$

3030w, 1563w, 1548w sh, 1477m, 1432s, 1422s sh, 1334w, 1308w, 1273m, 1238m, 1183m, 1154w, 1122vw, 1100w sh, 1079m, 1033vw sh, 1018w, 996m, 972vw sh,

Table 1 continued

933w, 922w sh, 845w, 790w sh, 738s, 683s, 662s sh, 614vw sh, 478s sh, 465s, 435m sh, 388m sh, 340s.

$Mo(S_2C_6H_4)_3$

3030w, 1520m, 1420m, 1306w, 1230m, 1160m, 1140w sh, 1068s, 1017m, 942w, 844w, 740s, 671m, 476m, 435w sh, 417w sh, 275m.

$W(S_2C_6H_3CH_3)_3$

3035w, 2910w, 2850w sh, 1585m, 1516m, 1460w sh, 1441m, 1372w, 1305vw, 1260w, 1242w, 1202s, 1152w sh, 1078s, 1030m sh, 950vw, 866m, 800s, 708vw, 692m, 650vw, 546m, 487w, 442m, 406vw, 373w, 337w.

$[(C_6H_5)_4As]\ Sb(S_2C_6H_4)_3$

3035m, 1572vw, 1543w, 1481m, 1437s, 1418m sh, 1337w, 1311w, 1260m, 1243m sh, 1185m, 1163w, 1157w sh, 1095m sh, 1081s, 1038w sh, 1021w, 998s, 972vw sh, 930w, 847w, 740s, 688s, 657m sh, 616vw, 479m sh, 467s, 433w sh, 348s.

Table 1 continued

$(C_2H_5)_4N\ I$

2980s, 2880m sh, 1460s, 1410s, 1410s, 1380m sh, 1316m, 1248w, 1184s, 1082m, 1027s, 1005m sh, 890vw, 870vw, 798s, 740vw sh, 630vw, 474vw.

$C_6H_3CH_3(SH)_2$

3054w sh, 3024w sh, 2954w sh, 2925m, 2869w sh, 2740vw, 2541m, 1892vw, 1820vw, 1743vw, 1594m, 1547vw, 1467s, 1383m sh, 1320vw, 1273m, 1218w, 1151w sh, 1129m, 1002vw, 972vw sh, 929w, 870m, 807s, 698w sh, 668m, 633w, 543m, 436m.

$C_6H_4(SH)_2$

3064m, 2544m, 1598w sh, 1575m, 1565w sh, 1457s, 1433s, 1408w sh, 1363vw, 1270m, 1165vw sh, 1120m, 1048m, 1012vw sh, 931m, 858vw, 748s, 662m, 435m.

$(C_6H_5)_4As\ Cl$

3045m, 3005w sh, 1625m, 1575w, 1475s, 1437s, 1338w sh, 1312m, 1278vw sh, 1260w, 1182w, 1159w sh, 1080s, 1021w, 995s, 927vw, 881w, 852vw, 800w, 754s, 740s sh, 688s, 614vw, 510m sh, 480s sh, 467s, 364s sh, 347s.

Table 1 continued

$(C_4H_9)_4N^+I^-$

2990s sh, 2950s, 2870s sh, 1465s, 1452s sh, 1404m sh, 1395m, 1379m, 1362m sh, 1322w, 1310w sh, 1239w, 1179w sh, 1164m, 1108m, 1066w, 1055w sh, 1038m, 989w, 921m, 895m, 879m sh, 794w, 736m, 532w, 400vw.

[a]Key: w, weak; m, medium; s, strong; br, broad; v, very; sh, shoulder.

Table 2: Conductivity and UV and Visible Spectra

Compound	Λ_m[a]	Band Maxima (cm^{-1})[b,c] (ε in parenthesis)
$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_3CH_3)_3$	213	12,300(271); 17,900(7130); 22,700(16,000); 30,000(18,000)
$[(C_2H_5)_2NH_2]_2\ Ti(S_2C_6H_3CH_3)_3$	143 53[d] 96[e]	12,400; 17,700; 22,700; 30,300
$[(C_2H_5)_4N]_2 Zr(S_2C_6H_3CH_3)_3$	230	27,800(11,400); 32,300 sh(21,000)
$[(C_2H_5)_4N]_2\ Zr(S_2C_6H_4)_3$	237	20,000 sh(2,030); 35,800 sh(25,200)
$[(C_2H_5)_4N]_2\ Hf(S_2C_6H_3CH_3)_3$	233	25,600 sh(5420); 33,100(18,400); 38,600(46,200)
$[(C_4H_9)_4N]\ Nb(S_2C_6H_3CH_3)_3$	104	17,200(10,700); 26,100(11,900)
$[(C_6H_5)_4As]\ Nb(S_2C_6H_4)_3$	85	17,700(10,700); 27,200(13,800); 30,700 sh(9120)

Table 2 continued

Compound	Λ_m[a]	Band Maxima (cm^{-1})[b,c] (ε in parenthesis)
$[(C_6H_5)_4As]$ $Ta(S_2C_6H_4)_3$	95	22,300(4,900); 28,700(14,500); 33,900(18,100)
$[(C_6H_5)_4As]$ $Sb(S_2C_6H_4)_3$		20,400(2460); 25,300(2210); 32,200(4940)

[a] molar conductivity in ohm^{-1} cm^2 $mole^{-1}$ for approx. 10^{-3} M CH_3CN solutions
[b] approx. 10^{-4} M CH_3CN solution
[c] key: sh, shoulder
[d] approx. 10^{-3} M CH_3NO_2 solution
[e] approx. 10^{-3} M acetone solution

cation, and when compared to the later prepared tetraethylammonium salt it was found to be essentially identical when the differences due to the cations were taken into account. The region from 700 to 250 cm^{-1} is particularly important for comparison, as this usually encompasses the metal ligand vibrations. The UV-visible spectra were also found to be independent of the cation. A ^{1}H-NMR of the product, Table 3, was obtained with great difficulty due to its low solubility in suitable solvents. The resulting integration seemed consistent with formula (I), except that the N-H signal could not be located. This problem is not surprising since, due to ^{14}N quadrupole broadening, it is difficult to locate this signal in $(C_2H_5)_2NH_2$ Cl, which is considerably more soluble. Also, a spurious peak was observed between 3 and 4 ppm downfield from TMS, which varied in position and intensity depending upon how well the solvent had been dried or whether or not TMS was added. Although this spurious signal could concievably be assigned to an S-H group, its variable position and intensity suggest that it is an impurity. Another disturbing fact about (I) was

Table 3: ^{1}H-NMR[a] and ^{13}C-NMR[b] Spectral Results[c]

	Solvent	NCH_3	NCH_2	CH_3	aromatic
$[(C_2H_5)_4N]_2Zr(S_2C_6H_3CH_3)_3$	d_6-DMSO	1.04 (24H,tt)	3.10 (16H,q	2.11 (9H,s)	6.3-7.0 (9H,m)
$[(C_2H_5)_4N]_2Zr(S_2C_6H_4)_3$	CD_6CN	1.05 (24H,tt)	3.06 (16H,q)		6.90 (12H,m)
$[(C_2H_5)_4N]_2$ $Nb(S_2C_6H_3CH_3)_3$	d_6-DMSO	1.08 (24H,tt)	3.10 (16H,q)	2.11 (9H,s)	6.3-6.9 (9H,m)
$[(C_2H_5)_2NH_2]_2$ $Ti(S_2C_6H_3CH_3)_3$	CD_3CN[d] (spurious peak at 3.6*)	1.03	3.02	2.13	6.4-7.0
$[(C_2H_5)_4N]_2$ $Zr(S_2C_6H_3CH_3)_3$ [a]	DMSO	6.9	51.4	20.2	122.0,128.3 129.2,146.8 150.1

Table 3 continued

[a]PPM downfield from internal TMS.

[b]PPM downfield from TMS as a secondary standard, with DMSO as primary standard using the shift of DMSO relative to TMS as 40.4 ppm. Recorded at 306 ^{0} K with proton decoupling.

[c]Key: s, singlet; q, quartet; m, complex multiplet; t, triplet; tt, triplet of triplets.

[d]Intensities are unreliable due to limited solubilities of ratio expected for the formulation shown. The spurious peak, marked by *, is presumably due to an impurity in the solvents, see text.

its conductivity (Table 2) which in several solvents seemed more characteristic of a 1 to 1 than a 2 to 1 electrolyte.[75] Similarly, a molecular weight of 334 was obtained in CH_3CN which is clearly consistent with 330 expected for a 1 to 1 electrolyte. However, concentration studies of the conductivity in CH_3CN and CH_3NO_2, Table 4, gave non-linear plots of the molar conductivity versus $\sqrt{C}$ thus suggesting that the low conductivity is a result of ion pair formation. The formation of ion pairs in this system would not be surprising as the cation could readily form hydrogen bonds to the anion sulfur atoms. However, it must be admitted that the product could actually be a 1 to 1 electrolyte such as $[(C_2H_5)_2NH_2]$ $Ti(S_2C_6H_3CH_3)_2(SC_6H_3CH_3SH)(HN(C_2H_5)_2)$ (II) which would contain two bidentate ligands and one monodentate ligand, with one dangling S-H group, and the sixth coordination site would be occupied by diethylamine. The somewhat more convincing nature of the IR and UV-visible evidence persuades us to favor (I) for the present time.

A reaction analogous to the above Ti reaction was also attempted with Zr, but the resulting red

Table 4: Concentration Studies of the Conductivity of $[(C_2H_5)_2NH_2]_2Ti(S_2C_6H_3CH_3)_3$

$10^3 \times c_m$[a]	Λ_m[b]	Solvent	$10^3 \times c_m$[a]	Λ_m[e]	Solvent
0.995	53	CH_3NO_2	0.150	198	CH_3CN
0.971	56	CH_3NO_2	0.300	177	CH_3CN
0.194	86	CH_3NO_2	0.600	155	CH_3CN
0.0971	109	CH_3NO_2	0.985	139	CH_3CN
			3.00	108	CH_3CN

[a] Moles-liter^{-1}
[b] cm^2 ohm^{-1} mole^{-1}

oil could not be obtained in crystalline form, nor could it be completely characterized.

Under the assumption that formula (I) was correct, and because of the difficulty encountered with Zr, it appeared worthwhile to investigate slight modifications of method I in order to produce six-coordinate 1,2-dithiolene complexes. Clearly it was desirable to avoid the diethylammonium cation and this could only be done by finding a strong base to initially remove two protons from the ligands as shown below:

$$2A^+B^- + 3(HS)_2C_6H_3CH_3 \longrightarrow$$

$$2A^+(SC_6H_3CH_3SH) + (HS)_2C_6H_3CH_3 + 2HB \qquad (11)$$

Reaction of the resulting mixture with a metal tetrakisamide should result in the desired complex with A^+ as counter ion, i.e. $A_2M(S_2C_6H_3CH_3)_3$. In early trials using n-butyllithium as the base, it was soon discovered that such a procedure (method 2) would work, although it worked well for only the very stable Ti and Nb complexes. The system was finally perfected when it was discovered that sodium cyclopentadienide, a reagent

readily available in good purity, could be used for preparing sodium salts of the ligands under totally anhydrous conditions. The sodium salts were also found to have the advantage that the sodium ion could readily be displaced in acetonitrile by addition of a tetraalkylammonium or tetraphenylarsonium chloride or bromide with concomittant precipitation of NaCl or NaBr. Thus, the general reaction of method 3, shown below, was developed.

$$M(NR_2)_x + (6-x)NaHS_2C_6H_3CH_3 + (x-3)(HS)_2C_6H_3CH_3 \longrightarrow$$

$$Na_{(6-x)}M(S_2C_6H_3CH_3)_3 \qquad (12)$$

(where M=Ti, Zr, and Hf,; x=4 and M=Nb and Ta, x=5)

Several general comments about the procedure must be made. First, although the tetraalkylammonium halides are largely insoluble in THF, it was evident that some exchange took place even under these conditions and so the practice of starting the exchange in THF was followed, as the tetraalkylammonium salts of the complexes appeared more stable than the alkali metal salts. Also, strict adherence to the stoichiometry of the reaction is obviously necessary as is the

exclusion of moisture, since most of the solutions are moisture sensitive. The 1 to 1 electrolytes were reasonably soluble in CH_2Cl_2 and slightly soluble in CH_3Cn, but the Ta complex decomposed in DMSO. On the other hand, the 2 to 1 electrolytes decomposed in CH_2Cl_2 but were stable in DMSO and CH_3CN.

The conductivity data, Table 2, do not require comment since values were clearly within acceptable ranges.[75]

The ^1H-NMR spectra, Table 3, were also consistent with the proposed formulations and are essentially identical to their main group congeners,[71] implying that the complexes are diamagnetic. The triplet of triplets observed for the CH_3 signal of the ethyl groups in the tetraethylammonium salts arises from coupling to the nitrogen (I=1), while the CH_2 protons display the usual quartet due to the relaxation of the N-H coupling by the nitrogen quadrupole.[76,77] This N-H coupling observed for the methyl groups is only seen in compounds where substitution about the nitrogen is highly symmetrical.

For further discussions, it will be worthwhile to consider recent structural studies carried out upon a number of the compounds reported here.[78]

The $Mo(S_2C_6H_4)_3$ and $Nb(S_2C_6H_4)_3^-$ complexes are trigonal prismatic, $Ta(S_2C_6H_4)_3^-$ is distorted from trigonal prismatic geometry, and $Zr(S_2C_6H_4)_3^{2-}$ and $Ti(S_2C_6H_3CH_3)_3^{2-}$ are close to octahedral geometry. Finer points of the geometry of these molecules will be considered in the next chapter.

Since the geometry of $Zr(S_2C_6H_4)_3^{2-}$ was close to octahedral, the ^1H-NMR of $Zr(S_2C_6H_3CH_3)_3^{2-}$ was studied because this stereochemistry should possess non-equivalent ring methyl groups. For octahedral geometry, one signal is predicted for the isomer with all methyls cis, and three signals due to the isomer with a cis, cis, trans arrangement, yielding a total of four peaks. However, the ring methyls displayed only one signal, and the solutions have not been cooled due to the low solubility of this complex. A ^{13}C-NMR was obtained to take advantage of the larger chemical shift differences expected for this technique. However, the ring methyls remained a singlet thus implying that there is either a very fast rearrangement occuring at room temperature, or that the all cis isomer is the only one present, or that the appropriate chemical shift differences are too small to observe.

Although infrared spectra were recorded from 4000 to 250 cm^{-1}, Table 1 and Figure 4, aside from their use in characterising the complexes, little structural information could be derived from them. The spectra are similar to the previously reported 2 to 1 complexes,[79] but strong coupling within the ligand system makes their interpretation difficult. If a total assignment of the various modes of vibration were available, it might be possible to correlate observed shifts with the amounts of dithioketone or dithiolate character of the ligands, as has been done for the simpler ethylenedithiol derivatives.[36] In the absence of such an assignment few conclusions can be made. The metal-sulfur stretching region of the spectrum does permit some correlations to be made however. In Table 5 and Figure 5 it may be seen that a change in geometry from trigonal prismatic to octahedral is accompanied by a reduction of the number of M-S vibrations, a shift of these vibrations to lower energy, and an increase in the intensity of the vibrations. The change in the number of vibrations is not surprising since symmetry arguments predict

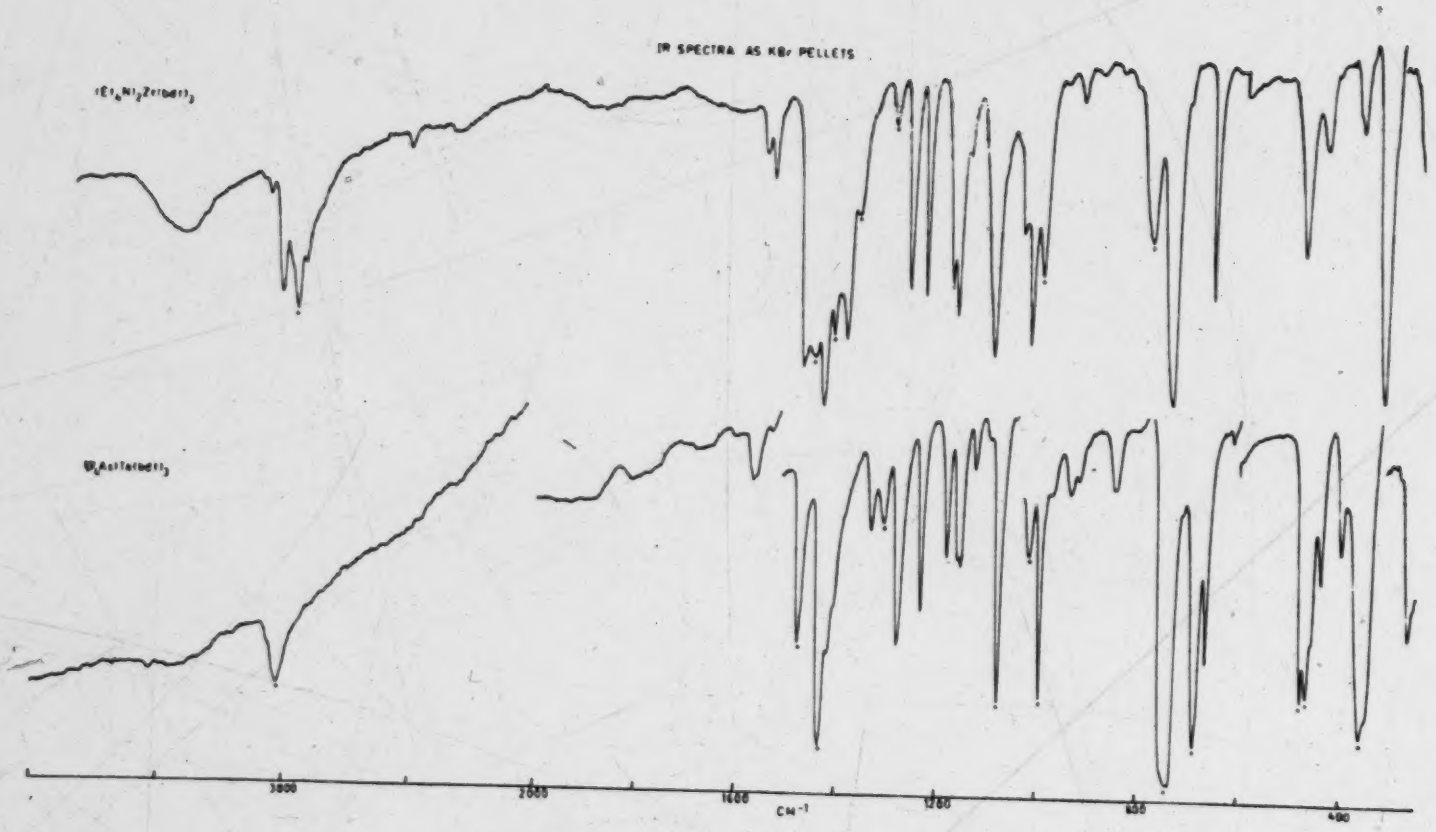


Figure 4: IR Spectra of Two Benzene-1,2-dithiolato Complexes.

Table 5: Metal-Sulfur Stretching Frequencies(cm^{-1})[b,c]

$[(C_2H_5)_4NH_2]_2\ Ti(S_2C_6H_3CH_3)_3$	393w sh, 382m, 356s, 336w sh
$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_3CH_3)_3$	392w sh, 382m, 354s, 336w sh
$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_4)_3$	392m sh, 388s, 343s
$[(C_2H_5)_4N]_2\ Zr(S_2C_6H_3CH_3)_3$	379w, 321s
$[C_2H_5)_4N]_2Zr(S_2C_6H_4)_3$	378w sh, 370w, 319vs, 304sh
$[(C_2H_5)_4N]_2\ Hf(S_2C_6H_3CH_3)_3$	377vw, 311s
$[(C_2H_5)_4N]\ Ta(S_2C_6H_3CH_3)_3$	392w, 339s
$[(C_6H_5)_4As]\ Ta(S_2C_6H_4)_3$	391m, 370-320s[a]
$[(C_6H_5)_4As]\ Nb(S_2C_6H_4)_3$	399m sh, 360s, 340sh[a]
$[(C_4H_9)_4N]\ Nb(S_2C_6H_3CH_3)_3$	398w, 364m, 336sh
$[(C_6H_5)_4As]\ Sb(S_2C_6H_4)_3$	340s[a]

[a]this region obscured by $(C_6H_5)_4As^+$
[b]Key: w,weak; m, medium;s, strong; v, very; sh, shoulder.
[c]Spectra as KBr pellets

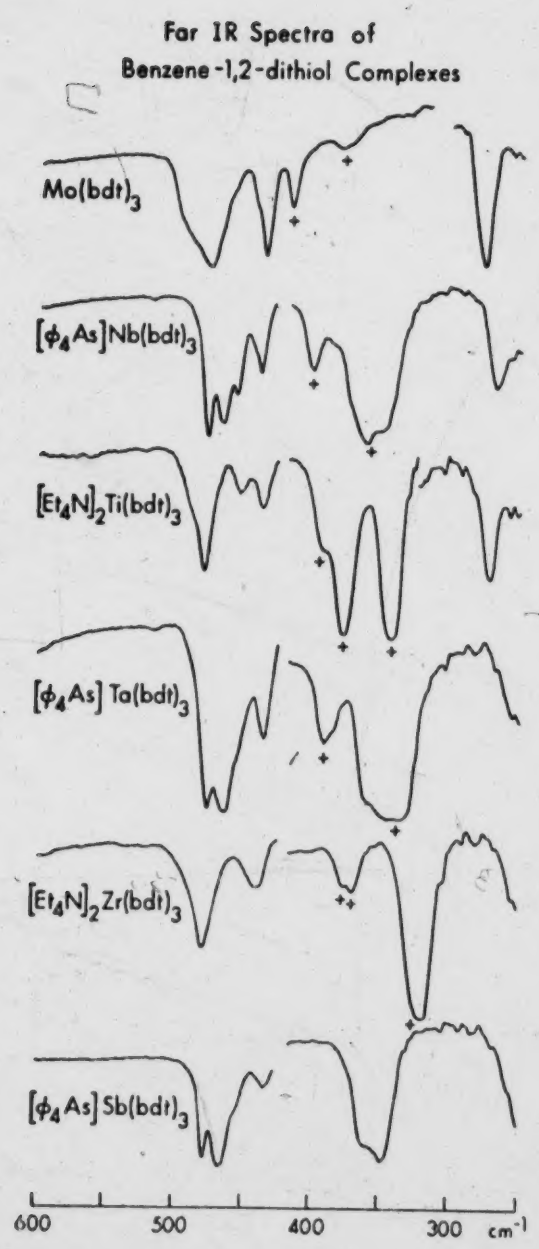


Figure 5: The Metal-Sulfur Stretching Region for Several Benzene-1,2-dithiolato Complexes. (+ indicates metal-Sulfur Stretch)

two bands for D_{3h} and one band for octahedral symmetry. The actual symmetries of the complexes are much lower, and thus the actual number of bands does not seem to have any significance. A problem with the above correlations arises in the Ti complexes which although octahedral display metal-sulfur stretches almost as high as Nb, but as will be seen later this is not the only place where the behaviour of complexes of Ti seems to be anomolous.

As pointed out in Chapter 1, the electronic spectra may often be of great use in predicting the geometry of 1,2-dithiolene complexes. However, not all of the compounds isolated in this work gave spectra indicative of trigonal prismatic geometry. Instead the observed bands shifted to higher energy in the manner:

$$Ti < Zr \sim Hf,\ Nb < Ta,\ Mo < Nb < Zr \text{ and } W < Ta < Hf.$$

Bennett pointed out that this is just the order in which the central metal d-orbital energies vary, while analyzing the results of a structural study of the Mo, Nb, and Zr complexes.[80] While this may not appear to be the proper order

for the metal d-orbital energies, it must be remembered that complexes as covalent as $TiCl_4$ may have an effective atomic charge as high as +1.8.[81] Thus, the effective atomic charge in these cases may be as high as +1.5 to +2.0, and the third ionization potential of each metal, Table 6, may be used to obtain a rough ordering of the d-orbital energies. As expected, the ionization potentials increase in the same order as the observed stabilization of the metal d-orbitals. It is then interesting to note that Schrauzer and Gray have assigned the lowest energy electronic transition to essentially ligand (π) ——> ligand (π^*) and ligand (π_v) ——> metal ($d_{x^2-y^2}$, dxy) transitions respectively. While the lack of metal ion dependence of the spectra of stilbenedithiol complexes thus far isolated seems to be consistent with the assignment of Schrauzer, it is obvious that the spectra of the benzenedithiol complexes behave in a manner more consistent with the results of Gray. The correlation of electronic spectra with metal d-orbital energies then suggested to Bennett and Cowie that the structural changes they had observed in their isoelectronic series; $Mo(S_2C_6H_4)_3$, $Nb(S_2C_6H_4)_3^-$ and $Zr(S_2C_6H_4)_3^{2-}$ might have been brought about by the destabilization

Table 6: Ionization Potentials[82] (eV)

Metal	I	II	III	IV	V
Ti	6.82	13.58	27.49	43.26	
Zr	6.84	13.13	22.99	34.34	
Hf	7.0	14.9	23.3	33.3	
V	6.74	14.65	29.31	46.71	65.23
Nb	6.88	14.32	25.04	38.3	50.55
Ta	7.89	16	22	33	45
Cr	6.766	16.50	30.96	49.1	70.2
Mo	7.099	16.15	27.16	46.4	61.2
W	7.98	18	24	35	48
Re	7.88	17	26	38	51

of the d-orbitals which would destroy delocalized bonding with the ligands, Figure 2. The prediction that destabilizing the d-orbitals should favor the octahedral geometry had already been made in the calculations favoring a σ -bonding model.[52] However, since a complete molecular orbital diagram was not given, it was difficult to say what effect the d-orbital energies would have upon the electronic spectrum.

Comparison of the electronic spectra of the series $Nb(S_2C_6H_4)_3^-$, $Ta(S_2C_6H_4)_3^-$ and $Sb(S_2C_6H_4)_3^-$ showed that it might be possible to test the relationship between d-orbital energy and structure by obtaining the Ta and Sb structures. The spectra of the latter compounds clearly indicate a distortion from trigonal prismatic geometry although the overall charge and metal ion size for the series are essentially constant. The structure of the Ta complex, to be described in Chapter 3, was not trigonal prismatic thus verifying the importance of the proper matching of metal d and ligand orbitals before trigonal prismatic geometry can occur.

In the converse argument it seems that the Ti spectrum is indicative of trigonal prismatic geometry. The fact that the Ti complex did not turn out to be trigonal prismatic shows that one must exercise caution in the interpretation of spectra of the first row transition metals. For some reason dithiolene complexes of these metals have spectra which are shifted to much lower energies than the analogous second and third row compounds. However, the prediction of trigonal prismatic geometry for Ti might also have been made from the metal sulfur stretching frequencies in the IR. Again, the stability of the Ti complexes, which is more like the Nb complexes than those of Zr, seems to indicate strong metal-sulfur bonds. It is possible that the high charge on the Ti complex is the cause of its octahedral geometry. On the other hand, the possibility that the first row transition metals strongly favor octahedral geometry because of their small size is certainly very real.

Recognizing the importance of the proper matching of metal and ligand orbital energies and the fact that an increase in the former may produce

distortions from trigonal prismatic geometry, it is interesting to ponder what effect decreasing the ligand orbital energies would have. Certainly, such a change must also produce distortions! If one accepts these arguments, it is not at all surprising that $W(mnt)_3^{2-}$, $Mo(mnt)_3^{2-}$ and $V(mnt)_3^{2-}$, where mnt-maleonitriledithiolate, all have geometries intermediate between the trigonal prism and octahedron. It has been previously suggested that the high charge and additional electrons in these complexes are responsible for the observed geometries.[53] The study of complexes such as $Mo(S_2C_6H_4)_3^{2-}$ or $Mo(S_2C_2Ph_2)_3^{2-}$ would be a great help in clarifying this question. The present reasoning favors trigonal prismatic geometries for these two compounds due to the somewhat higher orbital energies of these ligands.

Finally, some attention should be paid to the polarographic results in Table 7. The limited redox behaviour of the new complexes is consistent with their being more like metal dithiolates than dithioketones, as a result of the high d-orbital energies of the metal. As dithiolates, reduction

Table 7. Half Wave Potentials for Reduction (volts)[f]

	CH_3CN[b]	CH_2Cl_2[c]
$[(C_2H_5)_4N]_2\ Ti(S_2C_6H_4)_3$	-1.71	a
$[(C_2H_5)_4N]_2\ Zr(S_2C_6H_3CH_3)_3$	-1.71	a
$[(C_6H_5)_4As]\ Nb(S_2C_6H_4)_3$[d]	a	-0.38[d]
$[(C_6H_5)_4As]\ Ta(S_2C_6H_4)_3$[d]	---	-0.71[d]
$Mo(S_2C_6H_4)_3$[e]	---	0.366[e]
	---	-0.232[d]
$[(C_6H_5)_4As]\ Sb(S_2C_6H_4)_3$	---	a

[a]No redox behavior observed

[b]Potentials are relative to a Ag|0.1M $AgClO_4$, 0.1M $(n\text{-}C_3H_7)_4NClO_4$ reference electrode.

[c]Potentials are relative to a Ag|0.41M $(n\text{-}C_4H_9)_4NPF_6$, 0.05M $(n\text{-}C_4H_9)_4NI$, saturated AgI as reference electrode.

[d]Corresponds to $M(S_2C_6H_4)_3^- + e^- \longrightarrow M(S_2C_6H_4)_3^{2-}$.

[e]Corresponds to $M(S_2C_6H_4)_3^0 + e^- \longrightarrow M(S_2C_6H_4)_3^-$.

[f]The Ti and Zr waves were highly irreversible, but the Mo, Nb and Ta waves were nearly reversible as determined by plotting the log $i/(i_d-i)$ vs. E.

becomes more and more unfavorable since electrons must be forced into vacant molecular orbitals which become more and more metal in character, while at the same time the metal orbital energies are increasing. Thus, the reduction potentials should become more negative in the order: Mo< Nb< Zr and Nb< Ta; just as they do. What then is the problem with Ti? The observed potential, in contrast to the IR and UV-visible spectra, is certainly consistent with the fact that this compound has a structure very similar to Zr, but the highly irreversible character of the reduction waves for both metals leaves some doubt as to what is happening. At the same time, one may wonder why no oxidation waves were observed for any of the complexes. In answer to this, it must be pointed out that the only 3 to 1 dithiolene complexes ever to be oxidized below the 18 electron configuration are those of V; thus the lack of oxidation observed here should not be considered surprising.

It is readily apparent, then, that while the synthesis of 1,2-dithiolene complexes of the early transition metals has answered some

questions, many new questions have been raised which require further investigations. Certainly the new synthetic route described here should be of value in these and other investigations.

CHAPTER 3: THE CRYSTAL STRUCTURE OF TRIS (BENZENE-1,2-DITHIOLATO) TANTALATE (V)

The observation of trigonal prismatic geometry in complexes of 1,2-dithiols and 1,2-diselenols has presented a strong impetus for the investigation of structures of tris chelate complexes. An elucidation of the factors which stabilize trigonal prismatic coordination has been the objective of many of these investigations and some answers have been found. Studies involving ligands of various bite sizes seem to be in agreement with predictions that small bite sizes favor trigonal prismatic geometry.[83] Also it has been observed that ligand constraints can be utilized to impose this geometry upon the metal, but the role of ligand field stabilization energy in stabilizing octahedral geometry cannot be overlooked even in these cases.[84-89] Oddly enough, complexes of 1,2-dithiols and 1,2-diselenols, for which trigonal prismatic geometry was first observed, appear to be the least well understood in respect to the forces stabilizing trigonal prismatic geometry. Both Gray and Schrauzer have pointed out that S-S bonding and highly delocalized bonding

between the metal and ligand π orbitals are important, but the relative ordering of these and other factors such as strong σ bonding, the overall charge of the complex, the metal ion size, and the ligand field stabilization has not been established. The problem is basically due to the lack of systematic studies in this area. The synthesis of complexes of dithiols with the early transition metals has provided a basis for more orderly study, thus Bennett and Cowie have investigated the isoelectronic series of compounds $Mo(S_2C_6H_4)_3$, $Nb(S_2C_6H_4)_3^-$, and $Zr(S_2C_6H_4)_3^{2-}$.[78] The Mo complex was trigonal prismatic, Figure 6, the Nb complex is a slightly distorted trigonal prism, Figure 7, and the Zr complex is approaching ocahedral geometry, Figure 8. Accompanying the gross geometrical changes in the series, the variation of several bond lengths in a systemic fashion was noted. In particular, it was evident that a variation in the amount of delocalized bonding was occurring. The S-C bond lengths of the benzenedithiolato ligands underwent an increase from 1.727 Å in Mo, to 1.746 Å in Nb, to 1.765 Å in

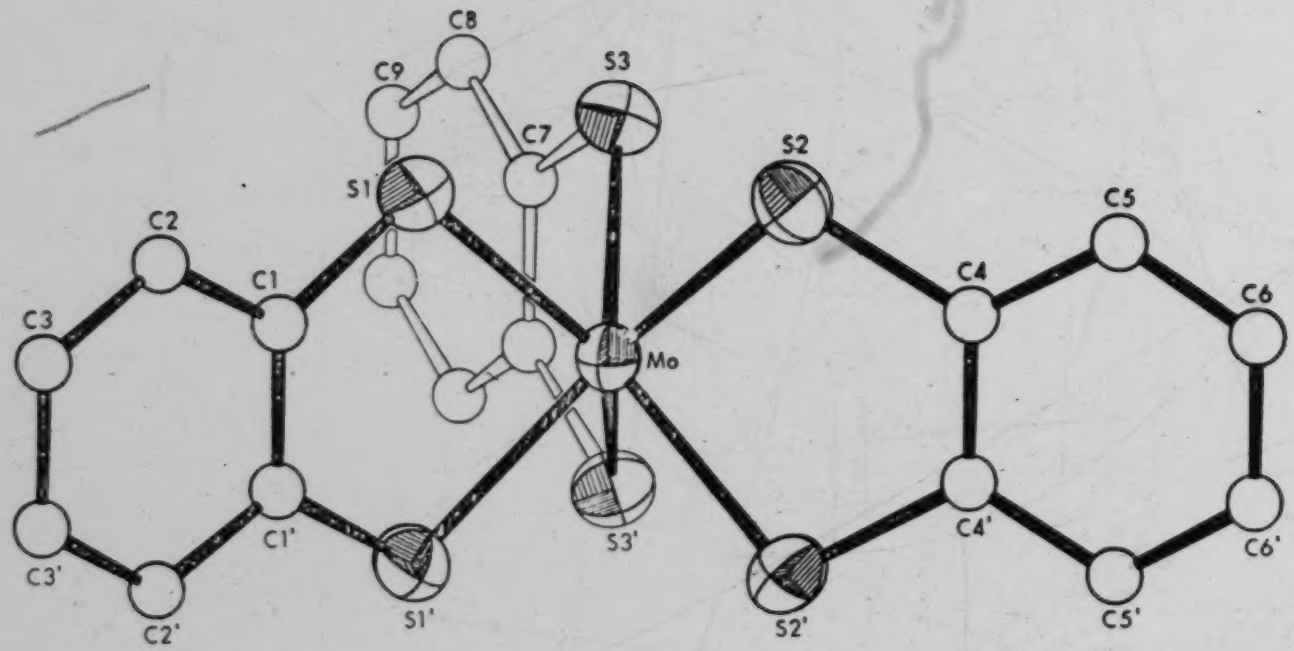


Figure 6: A View of $Mo(S_2C_6H_4)_3$.

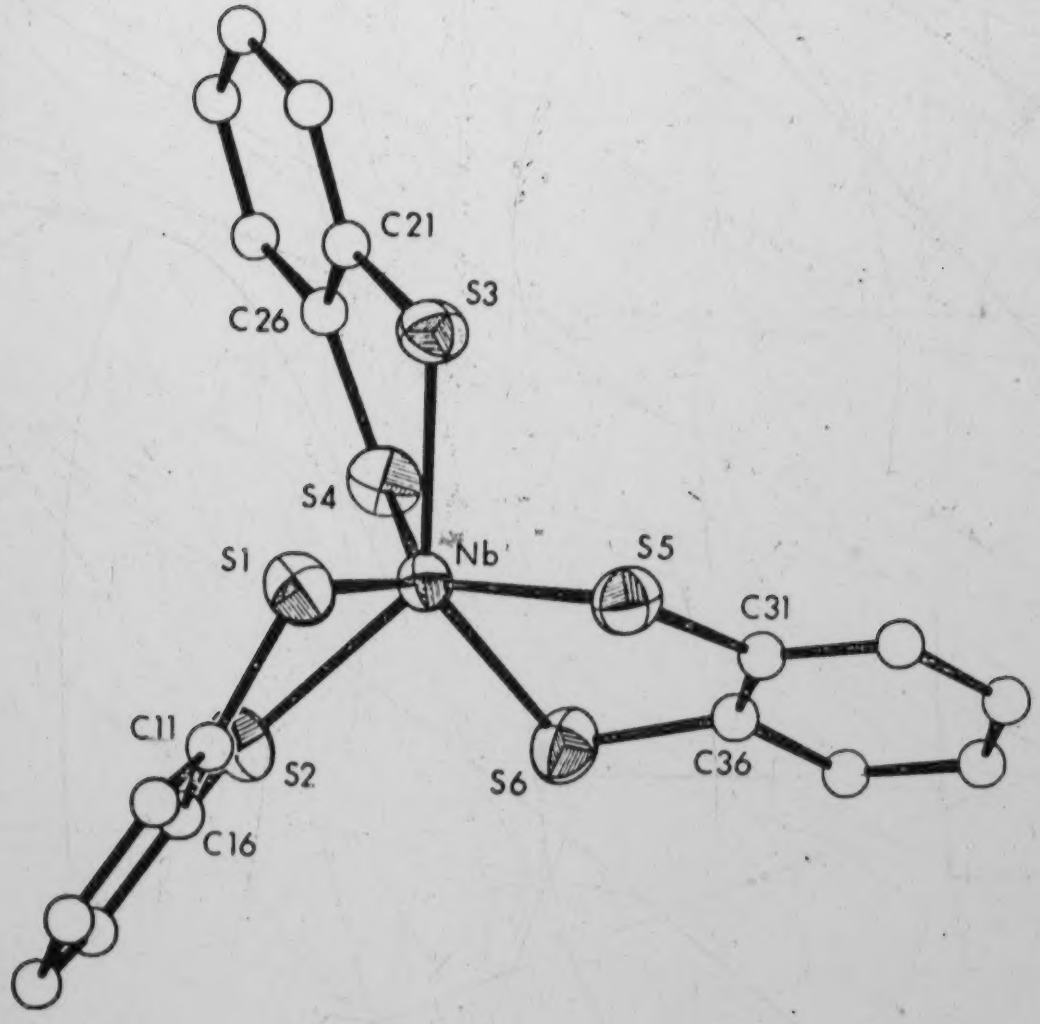


Figure 7: A View of $Nb(S_2C_6H_4)_3^-$.

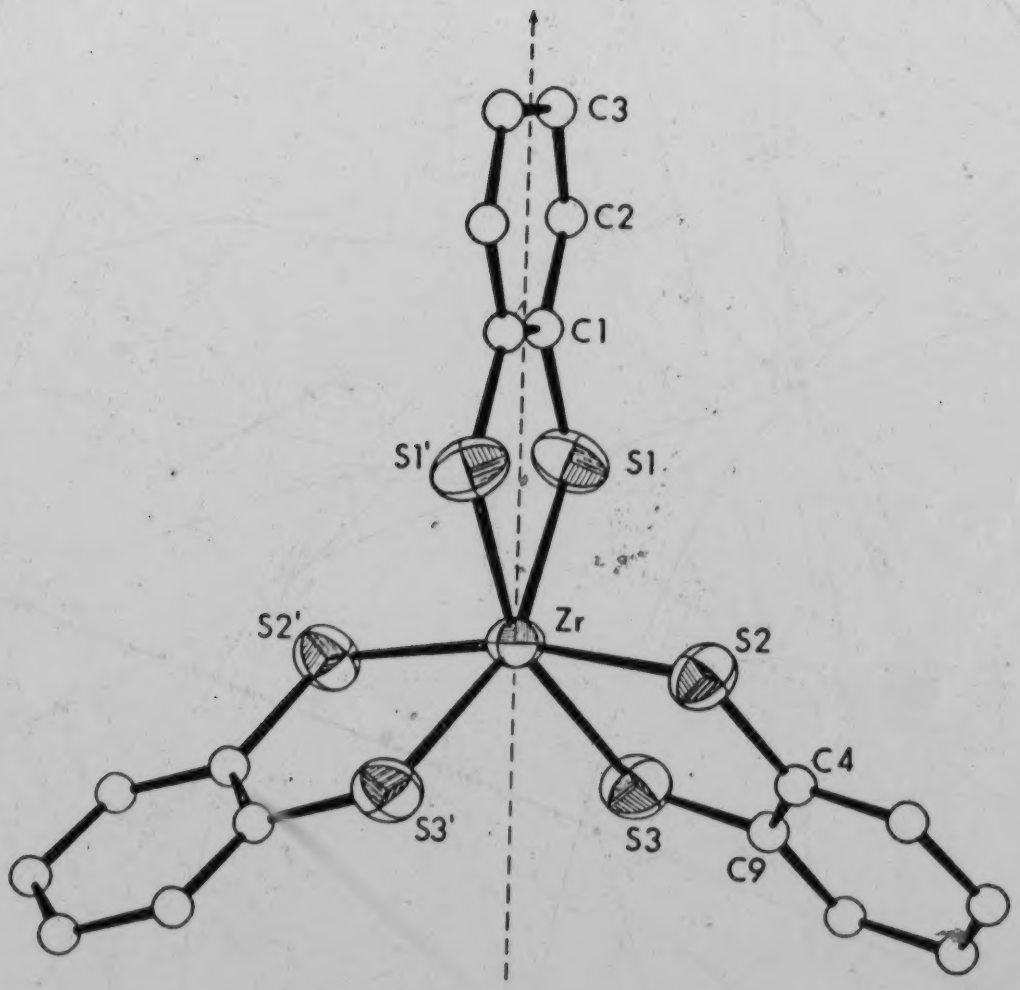


Figure 8: A View of $Zr(S_2C_6H_4)_3^{2-}$

Zr. These changes could be interpreted as an increasing importance of the dithiolate ($S_2C_6H_4^{2-}$) resonance form in the order Mo < Nb < Zr, and it was even suggested that the dithiolate form dominates in Zr. Unfortunately, the limitations of the structures did not permit high precision in the C-C bond lengths in the ligand systems so that the same trend was difficult to observe in these bonds. Nonetheless, Bennett and Cowie suggested that the observed structural changes resulted from an increase in the d-orbital energies of the central metal ion which consequently destroyed the highly delocalized bonding in the complexes. While the trend observed for the M-S bonds is consistent with the σ -bonding model, without a complete calculation of the bonds of the ligand system it is difficult to say whether this model would reproduce the observed trend in C-S bond lengths. At the same time it is obvious that other factors could be operating to disfavor trigonal prismatic geometry. The metal size was evidently increasing from Mo to Zr which, combined with the higher overall charge of the complex, would result in diminished S-S bonding

which favors the prism. Indeed, a rapid increase in interligand S-S distances was observed for the series. However, Cowie pointed out that the interligand S-S distances in the Nb complex, 3.232 Å, are longer than in any previously observed trigonal prism and are even longer than in the near octahedral $Mo[S_2C_2(CN)_2]_3^{2-}$. Further it may be pointed out that the expected increase in the M-S bond length from Mo to Zr based upon ionic radii[90] would be 0.12 Å, while the observed increase is about 0.17 Å. Thus it seems that the interligand S-S bonding may not be the major factor in stabilizing trigonal prismatic geometry.

Based upon spectroscopic evidence, we observed that the series of complexes: $M(S_2C_6H_4)_3^-$ (M=Nb, Ta, Sb), should show a distortion from trigonal prismatic geometry in the order given. Because the central metal ion size and overall charge of the complex remain essentially constant for the series, this observation has an important bearing on the point raised by Bennett and Cowie and on the question of prism stabilization by 1,2-dithiols. Furthermore, the reliability of predictions based upon spectroscopic

evidence has recently been called into question by the study of the closely related $Mo(MNT)_3^{2-}$ and $W(NMT)_3^{2-}$, where MNT= maleonitriledithiolate.[53] Despite the spectral differences of the two compounds, they were found to be essentially isostructural. Thus, we had an additional incentive to examine the structure of at least the Ta complex.

Experimental

$[(C_6H_5)_4As]Ta(S_2C_6H_4)_3$ Data Collection

Dark brown crystals were prepared as described in Chapter 2. Weissenberg photographs using CuKα radiation and precession photographs using MoKα radiation indicated $\bar{1}$ Laue symmetry with no systematic absences. Least squares refinement of 24 reflections with $35^0 < 2\theta < 50^0$ (MoKα[1], $\lambda = 0.70926$ A), automatically centered on a Picker automatic four circle diffractometer, yielded the cell dimensions and errors a=9.442(1), b=9.752(1), c=11.872(2), $\alpha=77.37(1)^0$, $\beta=71.20(1)^0$, $\gamma = 74.23(1)^0$ and $V=985.40$ A^3. The calculated density based on a formula weight of 984.98 a.m.u. was 1.66 g-ml^{-1} for one formula weight per unit cell compared to 1.67(2) g-ml^{-1} by flotation in a

mixture of CCl_4, CBr_4. Thus due to the lack of a center of symmetry in the tetraphenylarsonium group, it seemed that the space group must be P_1. A cell reduction by a known method[91] was attempted but the cell chosen was found to be a reduced cell.

The crystal fragment used resembled a distorted square pyramid with an overall height of 0.284 mm; the crystal faces were approximated by {0,1,1} ; { 1,0,0 }; { $\bar{1}$,0,$\bar{3}$ }; { 1,$\bar{2}$,2} and{$\bar{5}$,$\bar{2}$,$\bar{2}$ }. Intensity data was collected using MoKα radiation (λ = 0.71069 A)[92] and a coupled 2θ - ω scan technique with a 2θ scan rate of 0.5 min^{-1} and a 2θ scan width which was corrected for α^1 α^2 dispersion. Stationary background counts were made for 40 sec at each end of the scan range. A set of 3 standard reflections was collected every 50 reflections and an additional set of 10 standard reflections was collected every 12 hours, but no evidence of decomposition was observed.

On a total of 3700 reflections with $2\theta < 50^0$ collected, 3532 or 95% with $I'_{obsvd} < 3\sigma$ (I) were considered observed. Standard deviations were calculated using a "p factor"[93] of 0.03. Two reflections at low angles, 0,0,1 and 0,0,$\bar{1}$ were

rejected due to unusual background counts.

Solution and Refinement of the Structure

From a Patterson map.[94] two possible As positions consistent with the Ta at (0,0,0) were readily apparent, one at (0.426, 0.393, 0.433), and the other related by a center of symmetry. Not knowing which enantiomer was correct, the former position was arbitrarily chosen as a starting point, and the scale factor was subsequently refined [95-97] leading to R_1=0.291 R_2=0.309. A difference Fourier at this point revealed 12 possible positions for the sulfur atoms, two pairs of which were barely resolved. The above positions were separated into two groups of 6 positions by arbitrarily choosing one as a starting point and eliminating the position generated from this by the false center of symmetry. In this way, two sets of 6 chemically reasonable sulfur positions were generated. One set seemed to be more intense than the other and this was chosen for further refinement. One cycle of full matrix least squares refinement with the Ta, As and 6S gave R_1=0.175 and R_2=0.222. However, the thermal parameter of one sulfur atom was anomalously large and was sub-

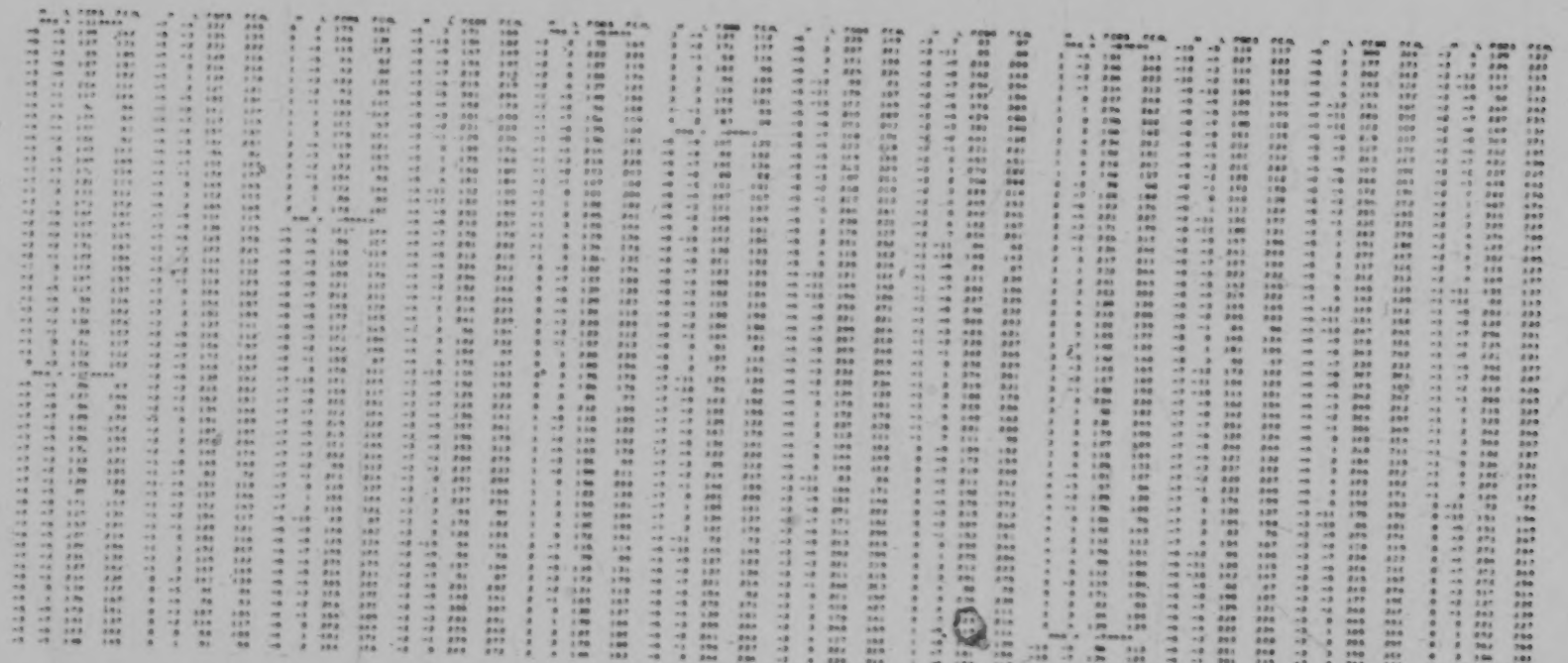
sequently lowered for an additional cycle of refinement. This sulfur atom again exhibited a high thermal parameter and so was removed before calculating another difference Fourier at which time R_1=0.154 and R_2=0.199. This Fourier map revealed the correct position for the remaining sulfur as well as the positions of the eighteen benzenedithiolate carbon atoms. An additional cycle of refinement including the new atoms gave R_1=0.121 and R_2=0.152. Another difference Fourier was needed to locate the tetraphenylarsonium carbon atoms. Including the tetraphenylarsonium phenyl rings as rigid bodies and adding anomalous dispersion corrections[100] yielded R_1=0.071 and R_2=0.082 after two cycles of refinement. Due to the highly irregular shape of the crystal fragment and the fact that μ= 39.68 cm^{-1}, an absorption correction was made on the basis of an experimental Phi scan. Transmission factors varied from 0.837 to 0.736. An additional cycle of refinement gave R_1=0.068 and R_2=0.081. Changing the enantiomeric form followed by two cycles of refinement yielded R_1=0.061 and R_2=0.073 which is a significant improvement at the 0.005

confidence level by a Hamilton R-factor test.[101] Adding all the Hydrogen atoms as rigid bodies with temperature factors 10-15% higher than the carbons to which they are attached and not refining their positions gave R_1=0.059 and R_2=0.072 after another cycle of refinement. Finally, using anisotropic temperature factors for Ta, As, 6S and 18 benzenedithiolate carbon atoms converged in two cycles of full matrix least squares refinement to the final values R_1=0.027 and R_2=0.031. The number of parameters being refined in the last two cycles was 280 and the shifts in all positional parameters were less than 1/2 the estimated standard deviation. The final standard deviation of an observation of unit weight was 1.466. A final difference Fourier revealed no peaks greater than 0.55e/Å^3. The observed and calculated structure factors are shown in Table 8.

Description of the Structure

The final positional and thermal parameters together with their estimated standard deviations are shown in Tables 9, 10, and 11. The closest cation anion contact is 2.72 Å between a tetraphenylarsonium

Table 8: Observed and Calculated Structure Factor Amplitudes.



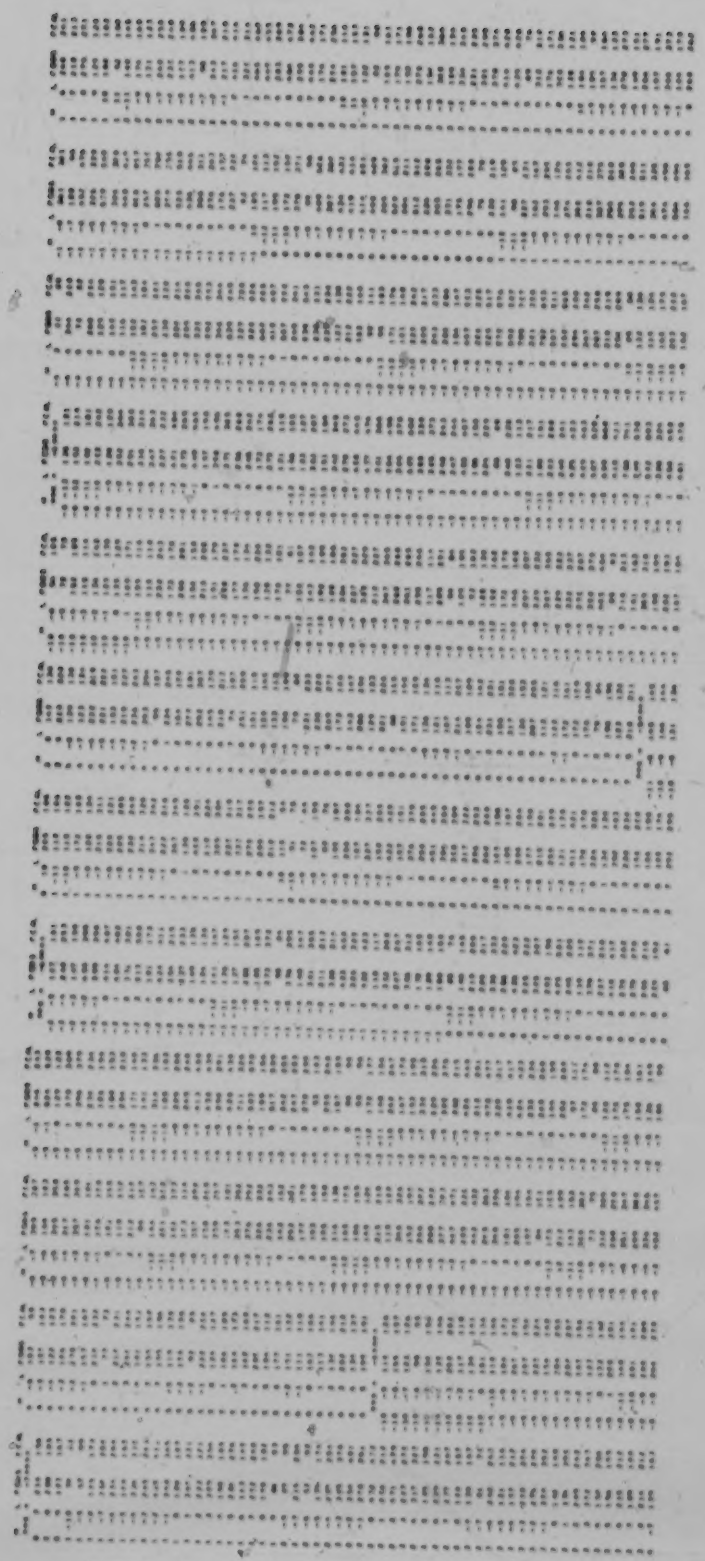


Table 8: Continued

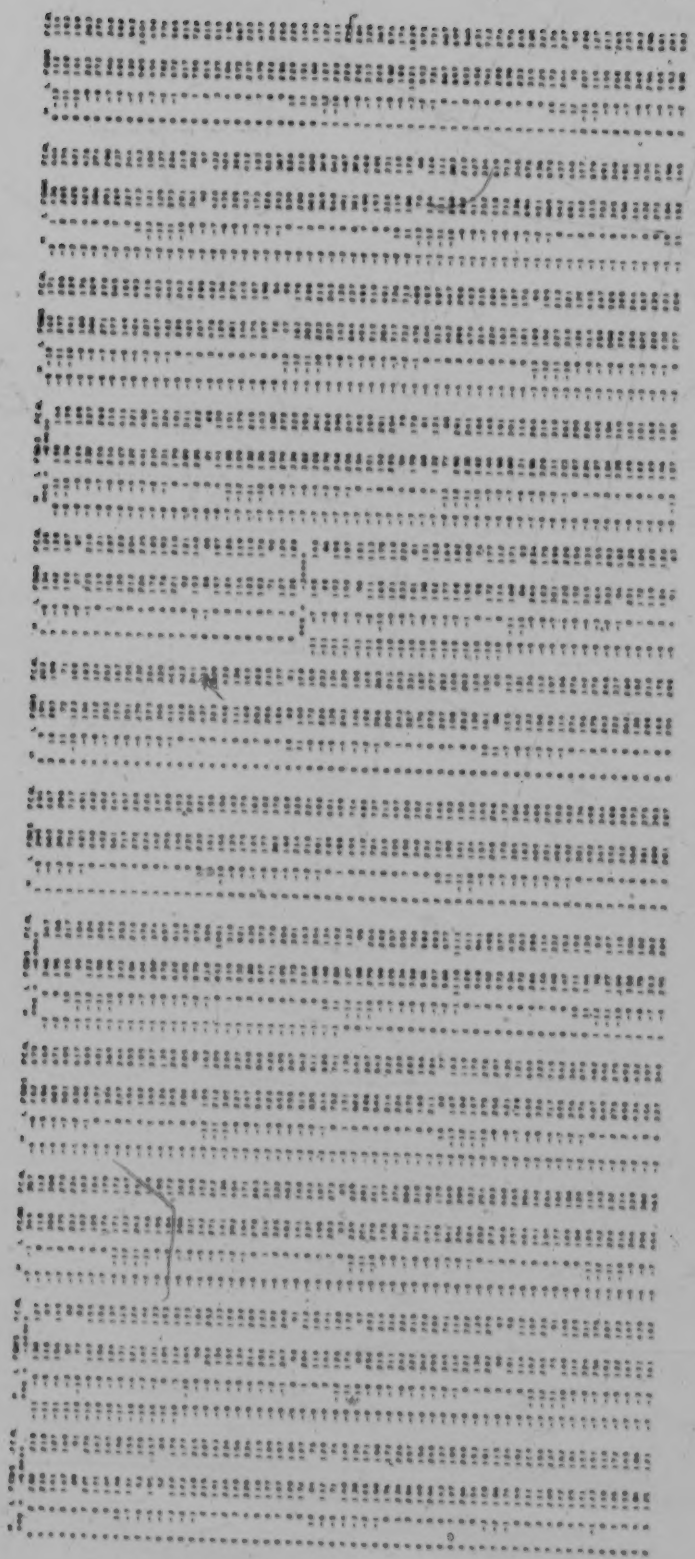


Table 8 continued

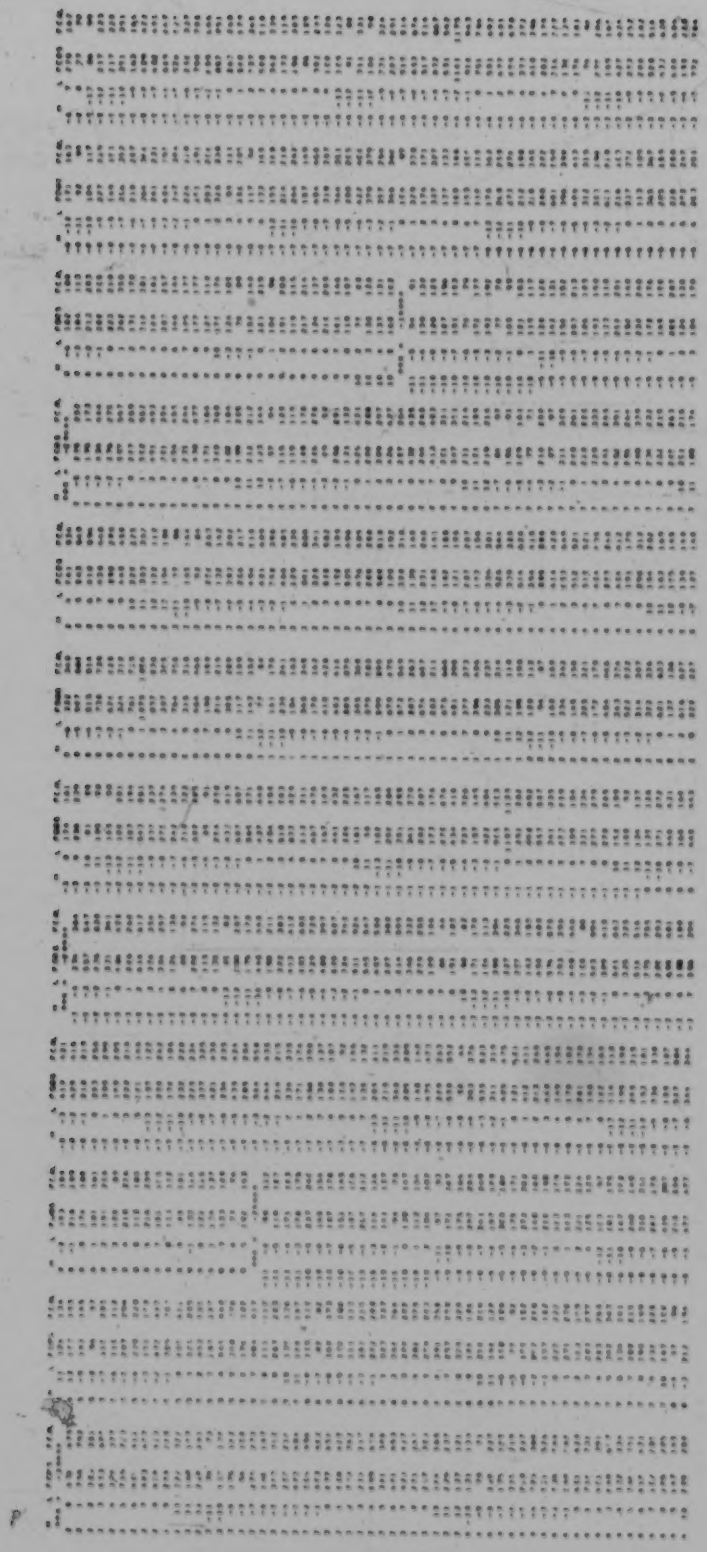


Table 8 continued

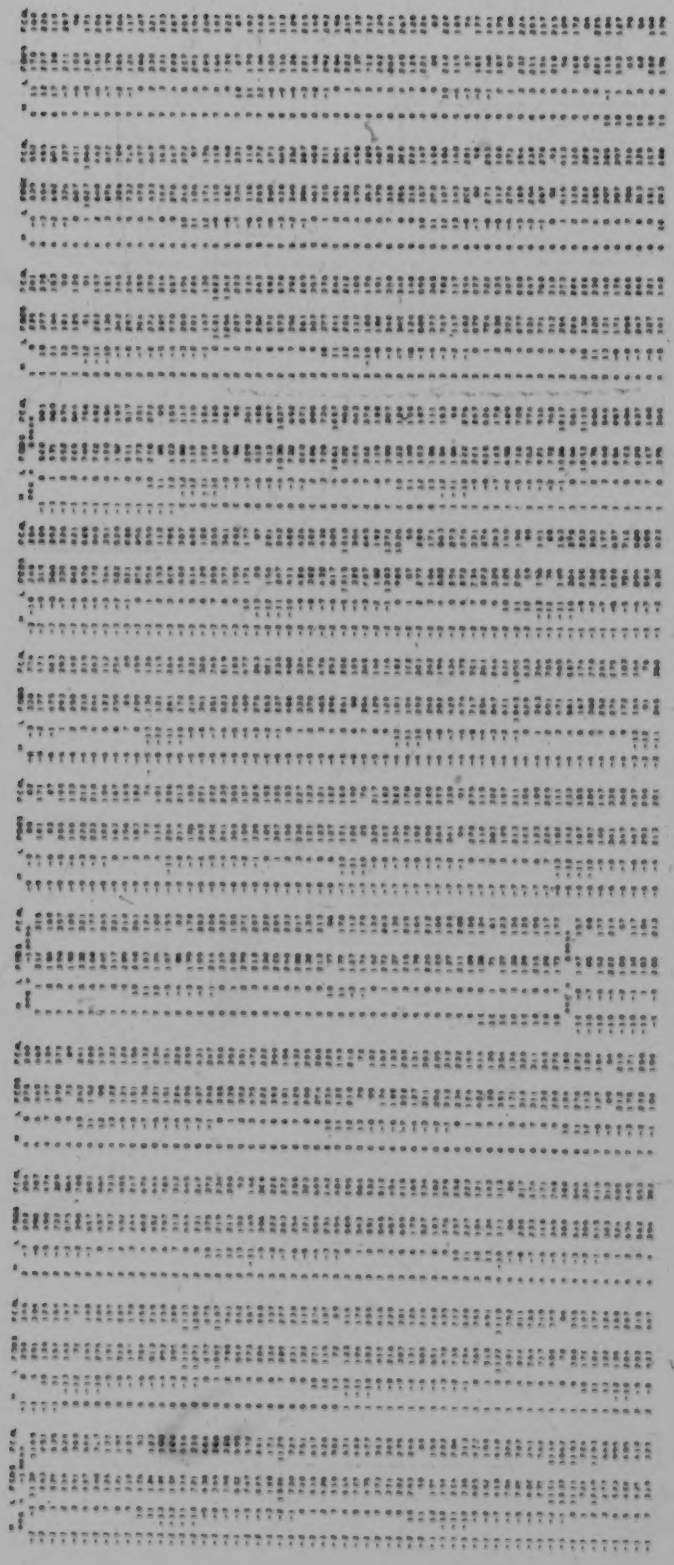


Table 8 continued

Table 9: Atom Coordinates and Isotropic Temperature Factors

Atom	x		y		z		B[a]
TA	0.0	(0)	0.0	(0)	0.0	(0)	3.84
AS	-0.43558	(8)	-0.39454	(9)	-0.44126	(6)	3.97
S1	-0.0537	(3)	0.2569	(2)	-0.0151	(2)	4.90
S2	0.0991	(3)	-0.2403	(3)	-0.0645	(3)	6.78
S3	0.2436	(2)	-0.0559	(3)	0.0412	(2)	5.07
S4	-0.2486	(3)	-0.0614	(3)	0.0465	(2)	5.60
S5	-0.0983	(2)	0.0322	(3)	0.2104	(2)	4.92
S6	0.0508	(3)	0.0645	(3)	-0.2184	(2)	5.33
C1	-0.0208	(9)	0.336	(1)	-0.I675	(8)	5.29
C2	-0.035	(1)	0.485	(1)	-0.198	(1)	6.64
C3	-0.007	(1)	0.546	(1)	-0.316	(1)	7.64
C4	0.033	(1)	0.461	(2)	-0.405	(1)	7.77
C5	0.050	(1)	0.316	(1)	-0.3751	(8)	6.13
C6	0.0233	(9)	0.251	(1)	-0.2555	(7)	4.83
C7	0.316	(1)	-0.239	(1)	0.0434	(7)	5.28
C8	0.444	(1)	-0.305	(1)	0.0859	(9)	6.82
C9	0.505	(2)	-0.446	(2)	0.089	(1)	9.16
C10	0.435	(2)	-0.530	(1)	0.050	(1)	9.17
C11	0.315	(2)	-0.471	(1)	0.005	(1)	8.16
C12	0.250	(1)	-0.320	(1)	-0.0014	(7)	5.28
C13	-0.2982	(9)	0.080	(1)	0.2351	(7)	4.77

Table 9 continued

Atom	x		y		z		B[a]
C14	-0.389	(1)	0.154	(1)	0.3279	(9)	6.87
C15	-0.548	(1)	0.186	(2)	0.352	(1)	8.17
C16	-0.609	(1)	0.135	(1)	0.282	(1)	7.57
C17	-0.523	(1)	0.067	(1)	0.191	(1)	6.49
C18	-0.3631	(9)	0.036	(1)	0.1641	(7)	4.79

[a]These are "equivalent" isotropic thermal parameters calculated from the anisotropic thermal parameters by SFLS5.

Table 10: Rigid Bodies

a) Phenyl Carbons

Atom	x		y		z		B
C19	-0.3777	(9)	-0.2608	(7)	-0.3805	(6)	3.98
C20	-0.4075	(8)	-0.2649	(7)	-0.2568	(7)	3.59
C21	-0.357	(1)	-0.1701	(7)	-0.2138	(4)	7.18
C22	-0.2760	(9)	-0.0713	(7)	-0.2945	(6)	6.75
C23	-0.2462	(8)	-0.0672	(7)	-0.4182	(7)	6.77
C24	-0.297	(1)	-0.1620	(7)	-0.4612	(4)	5.94
D	3.657	(4)					
E	1.422	(5)					
F	0.968	(4)					
C25	-0.275	(1)	-0.4670	(8)	-0.5735	(4)	4.11
C26	-0.197	(1)	-0.6105	(7)	-0.5598	(7)	5.03
C27	-0.0783	(8)	-0.6654	(6)	-0.6557	(6)	6.49
C28	-0.039	(1)	-0.5766	(8)	-0.7652	(4)	6.97
C29	-0.117	(1)	-0.4331	(7)	-0.7789	(7)	8.40
C30	-0.2356	(8)	-0.3782	(2)	-0.6831	(6)	7.49
D	5.849	(5)					
E	0.812	(5)					
F	2.910	(4)					
C31	-0.4734	(7)	-0.5529	(5)	-0.3207	(5)	3.47
C32	-0.3667	(7)	-0.6157	(6)	-0.2554	(4)	3.67
C33	-0.3855	(8)	-0.7389	(5)	-0.1711	(4)	4.68
C34	-0.5111	(7)	-0.7992	(5)	-0.1521	(5)	5.04

Table 10 continued

Atom	x		y		z		B
C35	-0.6178	(7)	-0.7364	(6)	-0.2174	(4)	5.40
C36	-0.5990	(8)	-0.6132	(5)	-0.3017	(4)	4.70
D	0.488	(3)					
E	2.493	(4)					
F	1.369	(3)					
C37	-0.609	(1)	-0.305	(8)	-0.4961	(5)	4.11
C38	-0.711	(1)	-0.1865	(8)	-0.4460	(7)	5.19
C39	-0.8384	(8)	-0.1175	(6)	-0.4884	(7)	7.04
C40	-0.863	(1)	-0.162	(8)	-0.5809	(5)	6.57
C41	-0.760	(1)	-0.2859	(8)	-0.6310	(7)	6.20
C42	-0.6331	(8)	-0.3548	(6)	-0.5886	(7)	5.17
D	2.301	(4)					
E	2.202	(6)					
F	2.688	(6)					

b) Phenyl Hydrogens[a]

Atom	x	y	z	B
H2	-0.0660	0.5463	-0.1331	7.2
H3	-0.0201	0.6529	-0.3381	8.4
H4	0.0529	0.5059	-0.4917	8.4
H5	0.0800	0.2524	-0.4403	6.7
D	3.029			
E	1.320			
F	3.702			
H8	0.4899	-0.2397	0.1155	7.4

Table 10 continued

Atom	x	y	z	B
H9	0.5955	-0.4910	0.1208	9.9
H10	0.4848	-0.6362	0.0512	9.7
H11	0.2684	-0.5300	-0.0235	8.8
D	5.971			
E	2.449			
F	2.358			
H14	-0.3414	0.1881	0.3785	7.5
H15	-0.6126	0.2377	0.4203	8.9
H16	-0.7259	0.1595	0.3004	8.3
H17	-0.5680	0.0316	0.1388	7.1
D	2.044			
E	3.093			
F	4.241			
H20	-0.4641	-0.3340	-0.2002	6.2
H21	-0.3778	-0.1724	-0.1273	7.9
H22	-0.2405	-0.0043	-0.2647	7.5
H23	-0.1895	0.0021	-0.4751	7.5
H24	-0.2758	-0.1596	-0.5481	6.6
D	3.656			
E	1.420			
F	2.017			
H26	-0.2252	-0.6728	-0.4831	5.6
H27	-0.0231	-0.7661	-0,6459	7.1

Table 10 continued

Atom	x	y	z	B
H28	0.0454	-0.6150	-0.8321	7.7
H29	-0.0881	-0.3706	-0.8556	9.2
H30	-0.2902	-0.2773	-0.6928	8.3
D	5.850			
E	0.809			
F	3.958			
H32	-0.2785	-0.5736	-0.2688	4.1
H33	-0.3105	-0.7833	-0.1255	5.2
H34	-0.5244	-0.8857	-0.0930	5.6
H35	-0.7062	-0.7784	-0.2039	5.9
H36	-0.6741	-0.5688	-0.3472	5.2
D	0.488			
E	2.495			
F	2.417			
H38	-0.6941	-0.1512	-0.3811	5.7
H39	-0.9104	-0.0338	-0.4534	7.6
H40	-0.9522	-0.1185	-0.6107	7.2
H41	-0.7777	-0.3207	-0.6958	6.8
H42	-0.5614	-0.4381	-0.6232	5.7
D	2.302			
E	2.202			
F	3.735			

[a]Hydrogens are numbered the same as the carbon atoms to which they are attached.

Table 11: Anisotropic Thermal Parameters $(A^2)^a$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	0.0483(2)	0.0434(2)	0.0468(2)	-0.01332(12)	-0.02001(12)	-0.00016(11)
As	0.0429(4)	0.0541(5)	0.0418(4)	-0.0107 (4)	-0.0101 (4)	0.0007 (4)
S1	0.0663(13)	0.0482(12)	0.0628(13)	-0.0125 (10)	-0.0304 (11)	-0.0032 (10)
S2	0.0848(18)	0.0614(16)	0.0958(20)	-0.0237 (14)	-0.0113 (15)	-0.0295 (15)
S3	0.0509(12)	0.0596(14)	0.0705(13)	-0.0097 (10)	-0.0249 (10)	-0.0037 (10)
S4	0.0611(13)	0.0784(16)	0.0651(13)	-0.0272 (12)	-0.0224 (10)	-0.0108 (12)
S5	0.0562(12)	0.0694(16)	0.0512(11)	-0.0068 (11)	-0.02734(9)	-0.0059 (11)
S6	0.0717(14)	0.0692(16)	0.0497(11)	-0.0236 (13)	-0.0179 (10)	-0.0019 (11)
C1	0.052 (5)	0.060 (6)	0.077 (6)	-0.021 (4)	-0.035 (4)	0.017 (5)
C2	0.073 (6)	0.054 (6)	0.111 (8)	-0.022 (5)	-0.047 (6)	0.022 (5)
C3	0.059 (6)	0.067 (7)	0.142 (10)	-0.027 (5)	-0.044 (7)	0.040 (7)

Table 11 continued

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C4	0.065 (6)	0.108 (10)	0.103 (8)	-0.042 (7)	-0.041 (6)	0.049 (8)
C5	0.047 (5)	0.100 (8)	0.071 (6)	-0.030 (5)	-0.022 (4)	0.015 (5)
C6	0.044 (4)	0.076 (6)	0.055 (5)	-0.027 (4)	-0.018 (4)	0.007 (4)
C7	0.067 (4)	0.066 (6)	0.042 (4)	-0.000 (5)	-0.001 (4)	0.008 (4)
C8	0.080 (7)	0.085 (8)	0.059 (6)	0.023 (6)	-0.006 (5)	0.000 (5)
C9	0.125 (11)	0.104 (11)	0.076 (8)	0.039 (9)	-0.022 (7)	-0.012 (8)
C10	0.153 (13)	0.065 (8)	0.068 (7)	0.042 (9)	0.012 (7)	0.013 (6)
C11	0.139 (11)	0.053 (7)	0.072 (7)	-0.014 (7)	0.031 (7)	-0.006 (5)
C12	0.076 (6)	0.047 (5)	0.047 (5)	0.002 (5)	0.010 (4)	0.009 (4)
C13	0.056 (5)	0.062 (5)	0.049 (4)	-0.010 (4)	-0.017 (4)	0.007 (4)
C14	0.065 (6)	0.112 (9)	0.064 (6)	-0.011 (6)	-0.000 (5)	-0.034 (6)
C15	0.073 (7)	0.101 (10)	0.106 (9)	-0.002 (7)	0.000 (6)	-0.029 (8)
C16	0.049 (6)	0.098 (9)	0.115 (9)	-0.015 (6)	-0.014 (6)	0.002 (7)

Table 11 continued

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C17	0.054 (5)	0.085 (8)	0.091 (7)	-0.019 (5)	-0.021 (5)	-0.001 (6)
C18	0.054 (5)	0.067 (6)	0.049 (4)	-0.021 (4)	-0.021 (4)	0.016 (4)

[a]The U's are the mean square amplitudes of vibration in angstroms from the general temperature factor expression: $\exp -2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell b^*c^*)$.

hydrogen and benzenedithiolato carbon atom. All non-hydrogen contacts exceed 3.30 Å.

The unit cell, Figure 9, was arbitrarily chosen with a Ta at each corner since the space group is P_1.

In the tetraphenylarsonium ion, shown in the center of Figure 9, the phenyl rings were treated as rigid bodies. The resulting geometry is in good argreement with other determinations [102,103] of this cation with average As-C bond distance, Table 12 being 1.889 Å while the C-As-C angles average 109.5°.

A stereo view of the $Ta(S_2C_6H_4)_3^-$ anion is shown alone in Figure 10. The important bond distances and angles consistent with the numbering scheme of Figure 10, are to be found in Figure 11 and Table 13. It is evident that the anion is distorted from the trigonal prismatic geometry found in the closely related Nb complex. The average ligand twist angle is 29°. However, the mode of distortion, unique among dithiolene complexes studied thus far makes such a statement meaningless since it tacitly implies a symmetric trigonal distortion of the two triangular faces, which is far from being

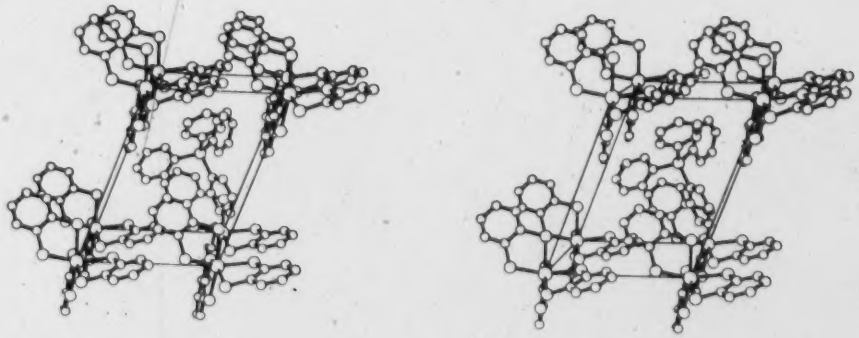


Figure 9: A Stereoview of the Unit Cell of $(C_6H_5)_4As\ Ta(S_2C_6H_4)_3$.

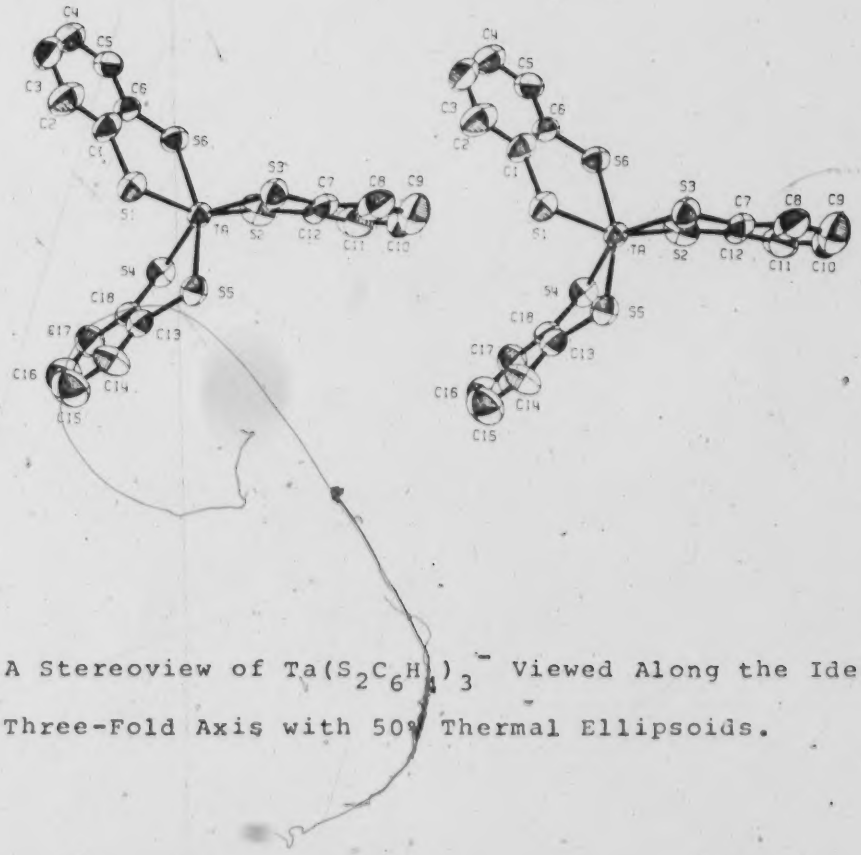


Figure 10: A Stereoview of $Ta(S_2C_6H_4)_3^-$ Viewed Along the Idealized Three-Fold Axis with 50% Thermal Ellipsoids.

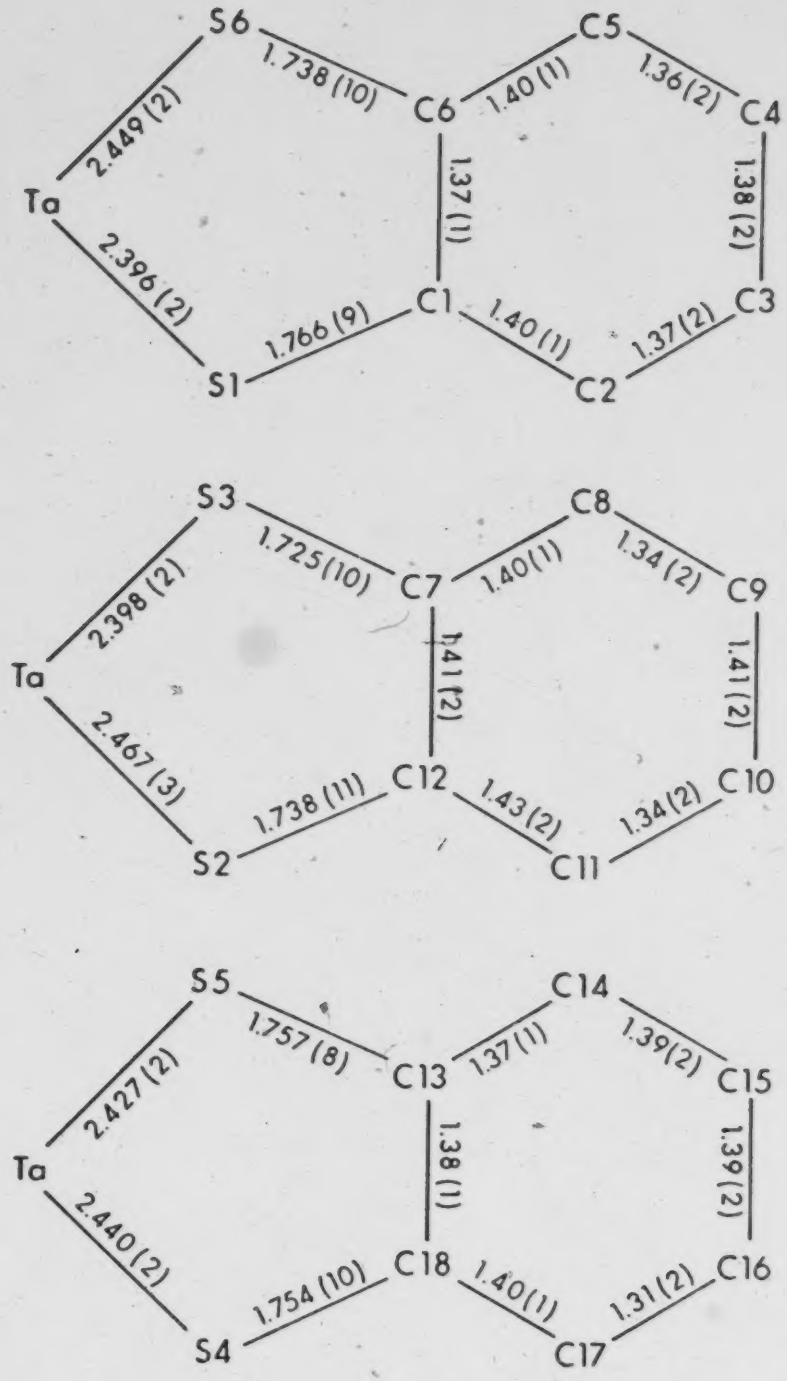


Figure 11: Bond Lengths for the $Ta(S_2C_6H_4)_3^-$.

Table 12: Intraionic Distances

Atoms		Distance (A)	Atoms		Distance (A)
Ta - S_{avg}	=	2.430	S_1 - S_3	=	3.646(3)
C - S_{Avg}	=	1.746	S_4 - S_6	=	3.722(3)
S - S(intra)	=	3.149	S_1 - S_5	=	3.059(3)
As - C_{Avg}	=	1.889	S_2 - S_6	=	3.132(4)
			S_3 - S_5	=	3.204(3)
As - C_{19}	=	1.890(5)	S_2 - S_4	=	3.265(4)
As - C_{25}	=	1.904(5)	S_1 - S_6	=	3.123(4)
As - C_{31}	=	1.888(4)	S_2 - S_3	=	3.177(4)
As - C_{37}	=	1.874(4)	S_4 - S_5	=	3.146(3)

Table 13: Intraionic Angles

Atoms	Angle, deg	Pair	Atoms	Angle, deg
S_1-Ta-S_5	78.73(9)	a	S_1-C_1-C_6	119.9(7)
S_2-Ta-S_6	79.15(10)	a	S_6-C_6-C_1	120.3(6)
S_1-Ta-S_6	80.29(9)		S_2-C_{12}-C_7	121.5(7)
S_4-Ta-S_5	80.52(7)	b	S_3-C_7-C_{12}	120.1(10)
S_2-Ta-S_3	81.52(9)	b	S_4-C_{18}-C_{13}	121.0(6)
S_2-Ta-S_4	83.42(9)	c	S_5-C_{13}-C_{18}	120.4(7)
S_3-Ta-S_5	83.20(7)	c		
S_1-Ta-S_3	99.02(8)	d	C_6-C_1-C_1	120.3(9)
S_4-Ta-S_6	99.15(8)	d	C_1-C_2-C_3	119.6(12)
S_1-Ta-S_4	105.42(8)	e	C_2-C_3-C_4	120.4(10)
S_3-Ta-S_6	106.36(8)	e	C_3-C_4-C_5	119.7(10)
S_2-Ta-S_5	122.28(10)		C_4-C_5-C_6	121.4(12)
S_3-Ta-S_4	147.19(8)		C_5-C_6-C_1	118.5(9)
S_5-Ta-S_6	158.09(8)	f	C_{12}-C_7-C_8	120.0(10)
S_1-Ta-S_2	158.69(8)	f	C_7-C_8-C_9	122.4(14)
S_1-S_3-S_5	52.57(7)	g	C_6-C_9-C_{10}	118.0(13)
S_2-S_4-S_6	52.77(8)	g	C_9-C_{10}-C11	122.1(12)
S_3-S_1-S_1	56.27(7)	i	C_{10}-C_{11}-C_{12}	120.9(14)
S_4-S_6-S_2	56.11(8)	i	C_{11}-C_{12}-C_7	116.5(11)
S_3-S_5-S1	71.16(8)	j	C_{18}-C_{13}-C_{14}	120.1(8)

Table 13 continued

Atoms	Angle,deg	Pair	Atoms	Angle,deg
S_6-S_2-S_4	71.12(9)	j	C_{13}-C_{14}-C_{15}	120.8(11)
			C_{14}-C_{15}-C_{16}	117.2(11)
Ta-S_1-C_1	110.1(4)		C_{15}-C_{16}-C_{17}	122.4(10)
Ta-S_6-C_6	109.4(3)		C_{16}-C_{17}-C_{18}	120.8(10)
Ta-S_2-C_{12}	104.9(4)		C_{17}-C_{18}-C_{13}	118.4(9)
Ta-S_5-C_{13}	103.9(3)			
Ta-S_3-C_7	108.0(4)		C_{37}-As-C_{31}	111.2(2)
Ta-S_4-C_{18}	103.4(3)		C_{37}-As-C_{19}	110.1(3)
			C_{37}-As-C_{25}	107.7(3)
			C_{31}-As-C_{19}	109.6(2)
			C_{31}-As-C_{25}	107.4(2)
			C_{19}-As-C_{25}	110.8(3)

true in the present compound. A clearer picture of the distortion is obtained by the individual chelate twist[104] or tilt[105] angles which are $\phi_{1,6} \approx 54^0$, $\phi_{2,3} \approx 16^0$, $\phi_{4,5} \approx 16^0$ and $\chi_{1,6} \approx 37^0$, $\chi_{2,3} \approx 10^0$, $\chi_{4,5} \approx 10^0$ (the subscripts refer to the sulfur atoms forming the chelate rings) respectively. It seems that part of the anion retains nearly the trigonal prismatic configuration, $\phi=0^0$, while the remaining chelate is close to the octahedral limit, $\phi=60^0$. In this regard, it is interesting to note that the "expected octahedral limit" based upon bite size and M-S bond lengths[83] is 49^0, and hence the most severely distorted chelate in our case has even passed this limit. Of course the above angle is for molecules which suffer symmetrical distortions, in particular keeping parallel triangular S_3 planes. This is not the case here, and the angle between the two planes is 11.8^0, allowing for the observed twist. The fact that part of the molecule retains a configuration close to that found in the trigonal prism is further evidenced by the angles S_2-Ta-S_5 of $122.28(10)^0$ and S_3-Ta-S_4 of

147.19(8) , which are close to 136° found in trigonal prismatic complexes. In addition, the dihedral angle, Table 14 , formed by the planes defined by Ta,S_2S_3 and Ta,S_4S_5 is 116.5°, again close to the expected 120° for a trigonal prism.

A comparison of some of the bond lengths and angles for the Mo, Nb, Ta, and Zr benzene-1,2-dithiolato complexes is shown in Tables 15 and 16. It is evident that the Ta complex lies between the Nb and the Zr complex from the S-M-S trans angle of 154.7° and the twist angle of 29°, The origin of the distortion in the Ta complex is, however, clearly not due to changes in the M-S bond length or the ligand geometry since these parameters are very close to the values found in the Nb complex. However, it must be recognized that the averages listed in Tables 15 and 16 were computed from values which cover a considerable range. For example, not too much significance should be attached to the average interligand S-S distance in the case of Ta since these vary from 3.059 Å to 3.722 Å. However, a clear trend is seen for several of the parameters as previously pointed out.

Table 14: Dihedral Angles

Atoms in Plane 1	Atoms in Plane 2	Angle
Ta,S_1,S_6	Ta,S_2S_3	107.6
Ta,S_1,S_6	Ta,S_4,S_5	106.4
Ta,S_2,S_3	Ta,S_4,S_5	116.5
Ta,S_1S_6	$S_1,S_6,C_1,C_2,C_3,C_4,C_5,C_6$	0.0
Ta,S_2,S_3	$S_2,S_3,C_7,C_8,C_9,C_{10},C_{11},C_{12}$	17.6
Ta,S_4,S_5	$S_4,S_5,C_{13},C_{14},C_{15},C_{16},C_{17}C_{18}$	30.0
S_1,S_3,S_5	S_2,S_4,S_6	11.8

Table 15: Summary of Distances for Benzenedithiolato Complexes

Compound	M-S	S-S(intra)	S-S(inter)	S-C
$Mo(S_2C_6H_4)_3$	2.367	3.110	3.091	1.727
$Nb(S_2C_6H_4)_3^-$	2.441	3.180	3.232	1.744
$Ta(S_2C_6H_4)_3^-$	2.430	3.149	3.338	1.746
$Zr(S_2C_6H_4)_3^{2-}$	2.543	3.265	3.584	1.765

Table 16: Summary of Angles for Benzenedithiolato Complexes

Compound	S-M-S(bite)	S-M-S(trans)	Projection Angle	Dihedral MS_2/ Ligand Angle
$Mo(S_2C_6H_4)_3$	82.18	135.7	0	13.1, 21.1, 30.0
$Nb(S_2C_6H_4)_3^-$	80.35	135.1	0.7	22.4
$Ta(S_2C_6H_4)_3^-$	80.78	154.7	29	0.0, 17.6, 30.0
$Zr(S_2C_6H_4)_3^-$	79.77	163.8	37	3.9,0.5

It would therefore be expected that the unique, highly twisted ligand in the Ta complex should exhibit long M-S and C-S bond lengths. Such is not the case, nor could any other sensible pattern be found for these bond lengths. The possibility remains that there is some systematic error present, possibly in the unit cell dimensions. However, all of the Ta-S bonds fall roughly along unit cell axes, and the alternating long-short pattern of lengths ($Ta-S_1$=2.396, $Ta-S_2$=2.467; $Ta-S_3$=2.398, $Ta-S_4$=2.440; $Ta-S_6$=2.449, $Ta-S_5$=2.427 Å) does not seem consistent with this type of error. Similar arguments can be made for other bonds of approximately the same orientation.

Again, the C-C bonds of the ligands did not fall into a simple pattern favoring either the dithioketone or dithiolate resonance structures. Even more than in the previous structures the Ta structure was plagued by high thermal motion which increased on going farther from the metal ion. Thermal motion was so large, in fact, that fuzzy "shadows" were associated with many of the spots in Laue photographs of the crystal. These "shadows" were assignable to thermal diffuse scattering by the

crystal.[106] As in the study of Bennett and Cowie, an anomaly was noted with the S atoms displaying larger or nearly as large thermal parameters as the C atoms to which they were attached.

Another interesting feature of the present structural study is the non-planarity of two of the benzenedithiolate ligand systems. As the twist angle varies from 16.3^0 and 16.5^0 to 53.7^0, the folding of the ligand system changes from 30.0^0 and 17.6^0 to 0.0^0. In $Zr(S_2C_6H_4)_3^{2-}$, the individual twist angles are $\phi_1 = \phi_2 = 42.8$ and $\phi_3 = 30.0$, while the corresponding ligand dihedral angles are 3.9^0 and 0.5^0; and in $Nb(S_2C_6H_4)_3^-$ where all three twist angles are near zero, the dihedral angles of the ligands are 22.8^0, 22.6^0 and 21.8^0. Similarly in $Mo(S_2C_6H_4)_3$, all twist angles are zero while ligand dihedral angles are 13.1^0, 21.1^0 and 30.0^0. It is difficult to understand why the nonplanarity of the ligand system is so variable, and for this reason it is tempting to ascribe these affects to packing forces; but at the same time the existence of a rough correlation between the twist angle and ligand bending must also be recorded. However, the direction

of this correlation seems to be just the opposite of what would be expected from the π-bonding argument. That is, π-bonding, which should favor the trigonal prism, should also favor planar ligands, i.e. the dithioketone resonance extreme and sp^2 hybridized S atoms. Further, it has been established previously that complexes of $S_2C_2(C_6H_5)_2$ have planar ligands, while $S_2C_2H_2$ is again bent. Ligand folding has also been observed in bis-cyclopentadienyl metal dithiolene complexes.[105-109] Arguments involving the affect of the metal and ligand substituents on the delocalization of bonding to the metal have been advanced by Kopf[107] and Kotoglu[108-110] in studies of biscyclopentadienylmetal dithiolate systems, where the ligand bending in $(\eta^5\text{-}C_5H_5)_2Ti(S_2C_6H_4)$[109] and $(\eta^5\text{-}C_5H_5)Ti(S_2C_6H_4)$[108] is nearly the same at 46°, whereas in $(\eta^5\text{-}C_5H_5)W(S_2C_6H_4)$[111] and $(\eta^5\text{-}C_5H_5)_2Mo(S_2C_6H_4)$[110] it is 8° and 9° respectively. The relationship of the $(\eta^5\text{-}C_5H_5)_2M(S_2C_2R_2)$ system to the tris dithiolene complexes is not clear at this time, but further work in one area could help clarify the other.

Discussion

The most important aspect of the Ta structure is that it varifies the contention of Bennett and Cowie that an increase in the d-orbital energy of the central metal results in a distortion from octahedral geometry. The fact that little change is seen in the M-S or C-S bond lengths only points out that the differences between Nb and Ta involve only small energy changes, as expected.

The nature of the distortion, which is unique among dithiolene complexes studied thus far, also deserves a word of comment. Although it is difficult to give an explanation for its occurence, an examination of existing structural data suggests that this type of distortion is not so unusual. In a recent discussion, Muetterties and Guggenberger favored the coordination polyhedron as a means of describing the geometry of complexes.[112] These authors pointed out that a tabulation of the angles between adjacent faces of the polyhedron will accurately describe the type of geometry. A large tabulation of these angles for complexes ranging from octahedral to trigonal prismatic coordination was presented. It then became apparent that

few complexes were known between the midpoint of this series and the trigonal prismatic limit. The Ta complex is then particularly important because it falls within this region. Table 17 presents the angles in question for the Ta complex. Comparison of these angles with those of Muetterties and Guggenberger brings out several interesting points. For complexes near the trigonal prismatic limit, δ's at b_1 vary considerably but often two are very similar, δ's at b_2 are nearly constant, and the remaining δ's may be grouped into three pairs of nearly equal angles. The reason for the observed pattern lies in the near C_2 symmetry of these complexes. The fact that the Ta complex has nearly C_2 symmetry is evident when comparing the intraionic angles in Table 13, which are lettered to identify pairs that would be related by a two-fold axis bisecting the chelate S_1S_6 and passing through Ta. Further examination of the angles of Muetterties and Guggenberger reveals that the deviation from C_3 symmetry increases as one approaches the trigonal prismatic limit. Thus complexes with small average twist angles such as $V(mnt)_3^{2-}$, $Mo(mnt)_3^{2-}$, $W(mnt)_3^{2-}$ and $Zr(S_2C_6H_4)_3^{2-}$

Table 17: Dihedral Angles Made by Polyhedron Faces[a]

δ's at b_1	δ's at b_2	Remaining δ's
24.2	90.3	59.6 , 60.5
48.8	92.7	81.0 , 82.7
49.3	95.3	87.4 , 89.8

[a] δ's are chosen as described in reference 112.

possess C_2 symmetry.[113] The deviation of many complexes from C_3 symmetry requires that individual twist or tilt angles or alternately Guggenberger's and Muetterties' δ's be reported and the reporting of average twist angles should be discouraged since it does not always give a clear picture of the distortion.

Also, some questions about the $D_{3d} \longleftrightarrow D_{3h}$ reaction path must be raised. While the energy differences between the Nb and Ta complexes must certainly be small, the average twist angle in the Ta complex, 29°, suggests that the Ta is well along the distortion path toward D_{3d} geometry. Does, then, the average twist angle truly indicate the position of a complex along the $D_{3d} \longleftrightarrow D_{3h}$ reaction path? Rather, the lack of examples lying between the midpoint and the trigonal prismatic extreme may not be a result of inadequate synthetic studies, but instead a result of the small energetic changes necessary to produce large distortions.

The unusual structural changes observed on going from Nb to Ta suggest that further work in this region of the periodic table with ligand systems of

slightly different energy, for example tetrachlorobenzenedithiol, would be well worthwhile for the purpose of increasing our understanding of the unusual bonding of 1,2-dithiolene complexes.

Table 18: Least Squares Planes[a]

Atoms Defining the Plane	Equation of the Plane	Distances of Atoms from the Plane (Å)
Ta, S_1, S_6	0.9952x-0.0542y -0.0815z=0	
Ta, S_4 S_5	-0.2576x+0.9307y- 0.2598z=0	
Ta, S_2, S_3	0.2407x+0.2872y- 0.9271z=0	
S_1, S_2, C_1, C_2	0.9937x-0.0962y- 0.0581z+0.0968=0	S_1 -0.007
C_3, C_4, C_5, C_6		C_3 0.026
		C_4 -0.012
		C_1 -0.019
		C_5 -0.012
		C_2 0.012
		C_6 -0.017
S_2, S_3, C_7, C_8	0.413x+0.0340y- 0.9099z-0.5479=0	S_2 0.046
C_9, C_{10}, C_{11}, C_{12}		C_9 0.037
		S_3 -0.025
		C_{10} -0.022
		C_7 -0.019
		C_{11} -0.029
		C_8 0.016
		C_{12} -0.014
S_4, S_5, C_{13}, C_{14}	0.0816x+0.7801y- 0.6203z+0.9075=0	S_4 0.006
		C_{15} 0.011
		S_5 -0.046
		C_{16} -0.048
C_{15}, C_{16}, C_{17}, C_{18}		C_{13} 0.032
		C_{17} -0.008
		C_{14} 0.021
		C_{18} 0.028
S_2, S_4, S_6	-0.6619x-0.4519y- 0.5981z-1.4608=0	

Table 18:continued

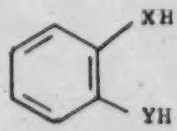
Atoms Defining the Plane	Equation of the Plane	Distances of Atoms from the Plane (Å)
S_1, S_3, S_5	0.6515x+0.6034y+ 0.4598z-1.4388=0	
S_1, S_4, S_5	-0.6462x+0.6447y+ 0.4085z-1.3948=0	
S_1, S_3, S_6	0.7283x+0.4472y- 0.5193z-1.2393=0	
S_1, S_4, S_6	-0.7426x+0.5336- 0.4048z-1.2551=0	
S_2, S_3, S_5	0.2257x-0.6918t+ 0.6859z-1.1519=0	
S_2, S_3, S_6	0.6553x-0.3714y- 0.6577z-1.3823=0	
S_2, S_4, S_5	-0.1936x-0.7029y+ 0.6844z-1.1573=0	

[a]The equations of the planes are Lx+My+Nz=D, where L, M, and N are direction cosines referred to the orthogonal coordinate system where x is a, y is in the ab plane, and z is c*.

CHAPTER 4: ORTHOMERCAPTOPHENOL AND 1,2-DIHYDROXY-BENZENE COMPLEXES

Introduction

In Chapter 2, a new method was presented for the synthesis of complexes of 1,2-dithiols. In this chapter the extension of this route to other ligands of the type I, where



(I)

X and Y are S,O and O,O will be presented. The method has permitted isolation of the following complexes: $[R_4E]_{6-x}M(XYC_6H_4)_3$, where M=Ti, Zr and Hf, x=4, $R_4E=(C_2H_5)_4N$, X=O and Y=S (also for Ti and Hf, X=Y=O); where M=Nb and Ta, x=5, $R_4E=(C_6H_5)_4As$, X=O and Y=S.

The complexes isolated here are important as analogs of benzene-1,2-dithiolate complexes, and as such may provide some new insight into the bonding in such systems. Also, it is to be noted that few complexes where X=O and Y=S have been reported in the chemical literature,[115,116] but during our investigations in this area, complexes of the type $H_xM(OSC_6H_4)_3$ (where x=2 for Ti and Zr, x=1 for Nb and Ta, and x=0 for W) were reported by other

researchers.[117] However, the Ti and Zr complexes were reported to undergo polymerization upon standing and were generally difficult to work with. Since the role of the hydrogens in these complexes was not clear, our investigations were continued because they have the advantage of producing well behaved crystalline materials. Similarly, with the complexes where X=Y=O, numerous reports have appeared on the synthesis of these complexes,[118-124] but again problems arise because of the presence of water or amines being associated with the samples, which were not prepared under rigorously anhydrous conditions. The difficulties which water of crystallization can cause is clearly illustrated by the dispute over a Si(IV) complex, where structures such as that shown in Figure 12 were considered possible.[125] Even a recent structure of the anhydrous pyridium salt $(C_5H_6N)_2\ Si(O_2C_6H_4)_3$ (C_5H_6N = pyridinium), showing the Si to be octahedrally coordinated by oxygen atoms,[126] does not answer questions about the hydrate. Therefore, we merely wish to demonstrate that anhydrous complexes may be prepared according to our method if this is desired.

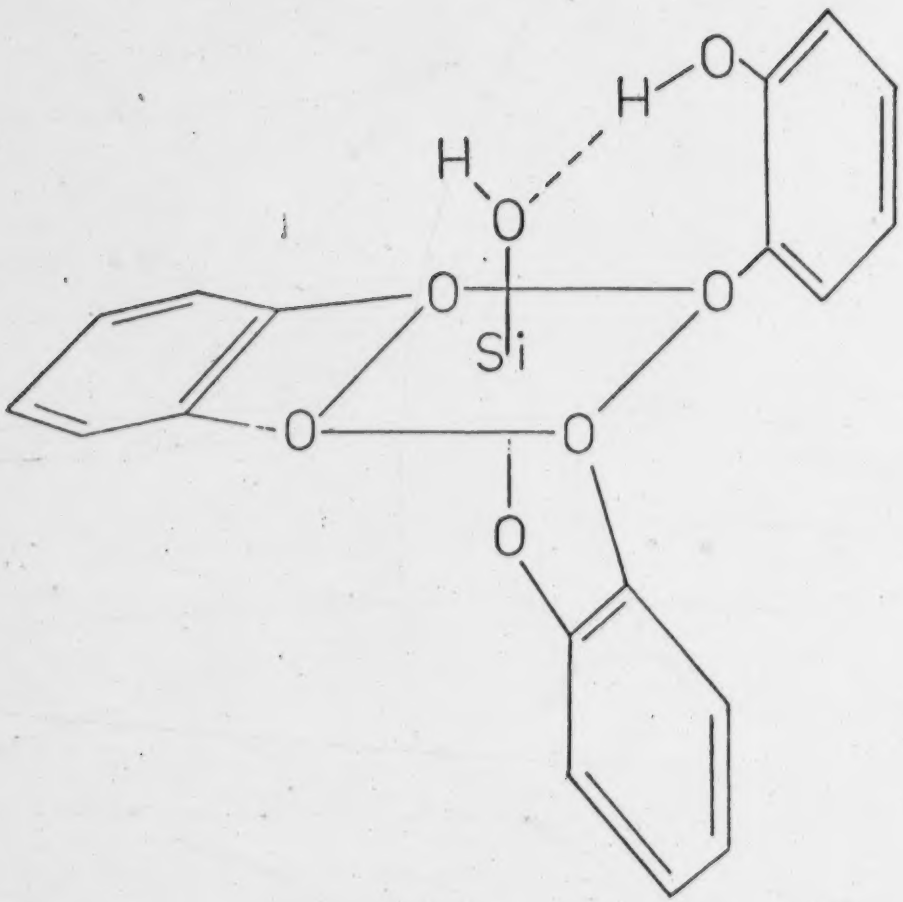


Figure 12: A Proposed Structure of a Hydrated 1,2-dihydroxybenzene Complex of Silicon.

Experimental

Much of the experimental technique used here has already been presented in Chapter 2, so discussions will be limited to new operations.

Tetraethylammonium chloride was purchased as a monohydrate and dehydrated at 80-90° C and 0.05 mm Hg. The anhydrous salt was then dissolved in CH_3CN and stored under nitrogen in a large reservoir with a buret attached to it for convenient measuring of the solution. The CH_3CN solution was standardized by precipitating the Cl^- as AgCl. The 1,2-dihydroxybenzene, or pyrocatechol, was obtained commercially and sublimed before use. Orthomercaptophenol was prepared according to U.S. patent 3,468,961 by permission of Hooker Chemical Corp., which was found to be superior to the previously preferred route.[127,128]

Preparation of the Compounds

$[(C_2H_5)_4N]_2\ Ti(OSC_6H_4)_3$

Sodium cyclopentadienide, 0.330 g (0.00375 mole), in 20 ml of THF was added to 0.00563 mole of o-mercaptophenol in 20 ml THF. Next, 0.00188 mole of $Ti[N(C_2H_5)_2]_4$ in 20 ml of THF was added, and after

stirring 48 hours, 13.8 ml of 0.272 M tetraethylammonium chloride in CH_3CN was added. This mixture was stirred 2 hours and then the solvent was removed under vacuum and replaced by 50 ml of CH_3CN. After stirring overnight the solution was filtered to remove NaCl. Addition of 55 ml of ether with vigorous stirring followed by allowing the solution to stand produced large black crystals. The reaction mixture was cooled in a freezer for 24 hours and the black crystals were filtered off, yield 0.518 g (40%). mp 218-220° uncorrected. Anal. Calcd: C, 59.98; H, 7.70; H, 4.11; S, 14.13. Found: C, 59.83, 60.07; H, 7.64, 7.74; N, 4.24, 4.24; S, 14.55, 14.59.

In a similar manner, the following compounds were also prepared.

$[(C_2H_5)_4N]_2\ Zr(OSC_6H_4)_3$

Pale yellow hexagons were obtained in 30% yield after one recrystallization. mp 218° uncorrected. Anal. Calcd: C, 56.39; H, 7.24; N, 3.87; S, 13.28. Found: C, 56.40, 56.47; H, 7.21, 7.56; N, 4.00, 4.12; S, 13.46, 13.18.

$[(C_2H_5)_4N]_2\ Hf(OSC_6H_4)_3$

White crystals, 77% yield, mp 214-215° uncorrected.

Anal. Calcd: C, 50.32; H, 6.46; N, 3.45; S, 11.85. Found: C, 50.86, 50.81; H, 6.75, 6.72; N, 3.40, 3.61; S, 11.58, 11.79.

$[(C_2H_5)_4N]_2\ Hf(O_2C_6H_4)_3$

White crystals in 34% yield. Anal. Calcd: C, 53.50; H, 6.87; N, 3.67. Found: C, 53.40; H, 6.49; N, 4.01.

$[(C_6H_5)_4As]\ Nb(OSC_6H_4)_3$

This complex was isolated by adding solid tetraphenyl arsonium chloride to the THF reaction. The THF was removed under vacuum after 2 hours and replaced by 50 ml of CH_2Cl_2 and after 2 hours the solution was filtered. Addition of ether and cooling produced black crystals in 60% yield which gave poor analysis. The product was recrystallized from hot CH_3CN to give black crystals, 24% yield. Anal. Calcd: C, 59.44; H, 3.80; S, 11.33. Found: C, 59.40; H, 4.29; S, 11.28.

$[(C_6H_5)_4As]\ Ta(OSC_6H_4)_3$

In the same manner as Nb, red crystals were obtained, 18% yield. Anal. Calcd: C, 53.88; H, 3.45; S, 10.27. Found: C, 53.38, 53.86; H, 3.58, 3.49; S. 10.04, 9.88.

$[(C_2H_5)_4N]_2\ Ti(O_2C_6H_4)_3$

This compound was prepared in the same manner as

the corresponding o-mercaptophenol complex except that diglyme was used as solvent instead of THF. After several recrystallizations from CH_3CN and ether mixtures orange crystals of suitable purity were obtained. Anal. Calcd: C, 64.55; H, 8.28. Found: C, 64.03; H, 7.80.

$[(C_6H_5)_4As]\ Nb(OC_6H_4(SH))_2Cl_4$

To 0.840 g (0.00665 mole) of o-mercaptophenol in 50 ml of THF was added 0.00229 mole of sodium cyclopentadienide in 12 ml of THF. Solid $NbCl_5$ was then added and the reaction mixture immediately turned dark brown. The reaction mixture was stirred for 96 hours after which 0.96 g of tetraphenyl arsonium chloride was added. After stirring for 1 hour the solvent was removed under vacuum and was replaced by 50 ml of CH_2Cl_2. After stirring 1 hour the mixture was filtered and 20 ml of ether was added resulting in the formation of a dark brown oil. The supernatant was decanted off and the oil was dried under vacuum but could not be characterized. An additional 20 ml of ether was added to the supernatant causing more oil to form. This time the reaction mixture was allowed to stand

for 1 week at room temperature and the oil dissappeared leaving black crystals. The IR of the product was very similar to $[(C_6H_5)_4As]\ Nb(OSC_6H_4)_3$, except for an additional peak at 800 cm^{-1} amd loss of a peak at 270 cm^{-1}. Yield: 19%, mp 196-198°.

Anal. Calcd: (for $[(C_6H_5)_4As]\ Nb(OC_6H_4SH)_2Cl_4$) C, 49.79; H, 3.48; S, 7.38; Cl, 16.33. Found: C, 50.39, 49.88; H, 3.54, 3.48; S, 7.06, 7.13; Cl, 16.82, 16.87. Physical Measurements were made as outlined in Chapter 2.

Results and Discussion

Sodium salts of the desired complexes were prepared in THF according to the following equation:

$$M(NR_2)_x + (6-x)NaXC_6H_4(YH) + (x-3)(HX)C_6H_4(YH) \longrightarrow Na_{(6-x)}M(XYC_6H_4)_3 \qquad (13)$$

(where x=4 for Ti, Zr and Hf and x=5 for Nb and Ta). As in the case of the benzene-1,2-dithiol complexes described in Chapter 2, the compounds were isolated as tetraphenylarsonium or tetraalkylammonium salts by exchange with the appropriate halide in CH_3CN or CH_2Cl_2. Some complications have arisen in the synthesis of the complexes of o-mercapto-phenol and 1,2-dihydroxybenzene, however. It appears

that, because of the higher solubility of NaBr and NaI in CH_3CN, the exchange is not as complete for bromides or iodides as it is for chlorides. While this caused no problems in the synthesis of benzene-1,2-dithiol complexes, the somewhat more forcing conditions necessary to precipitate the o-mercaptophenol and 1,2-dihydroxybenzene complexes may result in precipitation of the unexchanged tetralkylammonium bromide or iodide. All of these difficulties were overcome by using tetraethylammonium chloride. Although most tetraalkylammonium chlorides have the disadvantage of being hygroscopic, we have found that they may be easily dehydrated and subsequently handled as CH_3CN solutions.

Another problem encountered with the 1,2-dihroxybenzene complexes, and which could conceivably be a problem with other ligands, was that the sodium salt of the ligand was insoluble in THF. This difficulty may be eliminated by using diglyme as solvent, as the sodium salt of 1,2-dihydroxybenzene was soluble in diglyme and was successfully used in this manner to prepare the Ti complex. However, it

was found that the reaction between metal amides and the sodium salt of 1,2-dihydroxybenzene will still proceed in THF, and thus the use of diglyme is unnecessary and even undesirable, for this ligand system, due to its high boiling point.

Since the preparation of metal amides is an added inconvenience in preparing metal complexes, an attempt was made to prepare the sodium salt of the Nb complex with o-mercaptophenol directly from $NbCl_5$. Again a mixture of the ligand and its sodium salt was prepared in THF, but instead of adding $Nb(NMe_2)_5$, $NbCl_5$ was added and the resulting dark brown mixture was refluxed for 44 hours. Under these conditions, no characterizable compounds could be isolated, but by doing the same reaction at room temperature for 96 hours, after the addition of tetraphenylarsonium chloride, black crystals were obtained with the formula $[(C_6H_5)_4As]Nb(OC_6H_4SH)_2Cl_4$, which seems to be a mixed chloro-orthomercaptophenolato complex.

The complexes reported in this chapter are well behaved, air stable solids with the exception of the o-mercaptophenol complexes of Zr and Hf. All of the 2 to 1 electrolytes are soluble in CH_3CN, and the 1 to 1 electrolytes in CH_2Cl_2 or CH_3CN.

The conductivity measurements, Table 19, are consistent with the proposed formulations and need no further comment.[76]

The IR spectra of the complexes, Table 19, are very complex, but are clearly consistent with the overall make-up of the complexes. Detailed analysis of the spectra cannot be performed at this time due to the absence of vibrational assignments for these ligand systems.

The comparison of electronic spectra of the complexes, run on 10^{-4} M solutions between 10,000 and 40,000 cm^{-1}, to those of the corresponding benzene-1,2-dithiol complexes is interesting. The maxima, shown in Table 19, undergo a hypsochromic shift in the same manner as observed in Chapter 2, i.e. Ti< Zr ~ Hf, Nb < Ta, Nb < Zr and W < Ta < Hf. The dependence of the peak positions on the central metal and the high intensity of the bands again identifies them as mainly ligand to metal charge transfer. By comparison of spectra of one metal with the different ligands we also obtain a hypsochromic shift in the order $C_6H_4S_2^{2-} < C_6H_4OS^{2-} < C_6H_4O_2^{2-}$, which is the order of increasing stability of the

Table 19: Conductivity Measurements and UV, Visible Spectra[b]

Compound	m[a]	Maxima cm^{-1} (ε)
$[(C_2H_5)_4N]_2\ Ti(OSC_6H_4)_3$	251	24,300(9330); 33,300(36,700)
$[(C_2H_5)_4N]_2\ Zr(OSC_6H_4)_3$	242	32,300(19,000)
$[(C_2H_5)_4N]_2\ Hf(OSC_6H_4)_3$	250	32,500(20,500)
$[(C_6H_5)_4As]\ Nb(OSC_6H_4)_3$	92	23,900(9190)sh; 27,800(13,400); 36,100(36,400)
$[(C_6H_5)_4As]\ Ta(OSC_6H_4)_3$	-	32,300(16,400), 40,000(39,500)
$[(C_2H_5)_4N]_2\ Ti(O_2C_6H_4)_3$	226	26,700(12,300); 37,000(12,600)
$[(C_2H_5)_4N]_2Hf(O_2C_6H_4)_3$	221	33,900(19,700)
$W(OSC_6H_4)_3$		15,400(3450); 21,800(7720); 24,400 (7810); 30,000(7000); 36,800(14,800)

Table 19 continued

Compound	m[a]	Maxima cm^{-1} (ε)
$(HS)_2C_6H_3CH_3$		30,800 (1250)sh; 33,900(5000)
$(HO)C_6H_4(SH)$		31,700(2000); 35,300(9800)
$(HO)_2C_6H_4$		36,400(2900)

[a]Molar conductivity ohm^{-1} cm^2mole^{-1}
[b]sh, shoulder

Table 20: IR Spectra[a]

$[(C_2H_5)_4N]_2Hf(O_2C_6H_4)_3$

3045msh, 3005m, 2980msh, 2945wsh, 2580vw, 1570w, 1475s, 1410msh, 1392m, 1368vwsh, 1324s, 1303wsh, 1240s, 1181msh, 1170m, 1144wsh, 1093m, 1016m, 1002msh, 893msh, 867m, 791s, 731s, 613s, 598ssh, 546vw, 490s, 337w, 263s.

$W(OSC_6H_4)_3$

3050vw, 1560m, 1433s, 1290wsh, 1253s, 2129s, 1150w, 1116w, 1059m, 1017m, 968vw, 930w, 850s, 742s, 719msh, 693s, 630s, 547s, 447s, 431ssh, 398ssh, 309m, 268w.

$[(C_2H_5)_4N]_2Ti(O_2C_6H_4)_3$

3040wsh, 2980w, 1561w, 1460s, 1392w, 1339w, 1327w, 1303vw, 1247s, 1182wsh, 1171w, 1143vw, 1092w, 1011w, 892w, 867w, 801m, 737msh, 727m, 623m, 600wsh, 553vwsh, 538vw, 502m, 410m, 320m.

$C_6H_4(OH)_2$

3450s, 3320s, 3050vw, 1618m, 1596msh, 1510s, 1468s, 1362s, 1278ssh, 1253s, 1239ssh, 1187s, 1164msh, 1149wsh, 1094s, 1039m, 935vw, 915w, 839m, 769msh, 754msh, 741s, 722vwsh, 630mbr, 567w, 559w, 495mbr, 450wsh, 378w, 335vw.

Table 20 continued

$[(C_6H_5)_4As]$ $Nb(OSC_6H_4)_3$

3044m, 1460w, 1480msh, 1438s, 1393wsh, 1335wsh, 1310wsh, 1254ssh, 1225s, 1184msh, 1163wsh, 1151wsh, 1114m, 1079m, 1065msh, 1020m, 996m, 920wsh, 849s, 737s, 722msh, 686s, 544s, 464ssh, 436s, 362s, 322msh, 270m.

$[(C_6H_5)_4As]$ $Ta(OSC_6H_4)_3$

3045m, 3000wsh, 1560m, 1479msh, 1436s, 1395wsh, 1333wsh, 1306wsh, 1252ssh, 1223s, 1181msh, 1160wsh, 1147wsh, 1111m, 1078m, 1063msh, 1019m, 995m, 918wsh, 862s, 741s, 720msh, 687s, 635s, 546s, 478msh, 465s, 438s, 371s, 306w, 252s.

$[(C_2H_5)_4N]_2Ti(OSC_6H_4)_3$

3018vwsh, 3046msh, 2982m, 2950msh, 2582vw, 1555m, 1479ssh, 1446s, 1432ssh, 1392ssh, 1368wsh, 1262s, 1235ssh, 1181msh, 1171m, 1147vw, 1109m, 1065m, 1028s, 1001msh, 913wsh, 851s, 787msh, 749s, 726msh, 691s, 622s, 549s, 430s, 368s, 300s.

$[(C_2H_5)_4N]_2Hf(OSC_6H_4)_3$

3055msh, 2990m, 2955wsh, 2570vw, 1566m, 1483ssh, 1453s, 1437ssh, 1496msh, 1371wsh, 1267s, 1237ssh, 1184msh, 1172m, 1149vwsh, 1109m, 1080vwsh, 10 1063m, 1028m, 1001msh, 915wsh, 860msh, 847m, 787msh, 751s, 728msh, 688s, 618s, 545m, 451wsh, 430m, 348m.

$[(C_2H_5)_4N]_2Zr(OSC_6H_4)_3$ n=nujol

3050-2760sn, 1563msh, 1555m, 1470-1430sn, 1375sn, 1303wsh, 1269s, 1232ssh, 1182msh, 1171m, 1148wsh, 1105m, 1074vwsh, 1061m, 1024m, 1001msh, 914w, 894vwsh, 846s, 784m, 746s, 724ssh, 683s, 613s, 548m, 448wsh, 427m, 344s.

HOC_6H_4SH

3430sbr, 3070w, 3030wsh, 2580wsh, 2530w, 1578m, 1490msh, 1473s, 1447ssh, 1339m, 1288m, 1240msh, 1204s, 1182ssh, 1155msh, 1128msh, 1073m, 1061wsh, 1035wsh, 1029m, 941vwsh, 925wsh, 913w, 832m, 751s, 711w, 692vwsh, 679m, 564vw, 497vw, 439w, 374w.

[a]Key: s, strong; m,medium; w,weak; sh,shoulder; br,broad; v,very.

ligand orbitals and is thus consistent with mainly ligand to metal charge transfer. However, it is interesting to note that the spectra of the W and Nb complexes of o-mercaptophenol bear a strong resemblance to some of the benzene-1,2-dithiol complexes known to be trigonal prismatic. Certainly the complexes of 1,2-dihydroxybenzene and o-mercaptophenol are expected to be close to the octahedral limit, but the spectra suggest that it cannot be taken for granted that the complexes are all octahedral. However, some structural studies should be undertaken before attempts are made to correlate the structures with the spectra.

Polarographic studies on the W and Nb o-mercaptophenol complexes were made in CH_2Cl_2 and the Ti 1,2-dihydroxybenzene complex was studied in both CH_2Cl_2 and CH_3CN, but in no case was either oxidation or reduction observed. The absence of oxidation is not surprising because the ligand orbitals are even more stable here than for benzene-1,2-dithiol, and no oxidation was observed for complexes of the latter ligand. However, it seems that if there is any ligand

character in the lowest unoccupied molecular orbital, the reduction potentials of 1,2-dihydroxybenzene and o-mercaptophenol complexes should be at more positive potentials than the corresponding benzene dithiol complexes. No explanation can be offered, at this time, for the absence of reduction waves. Further investigations with a dropping mercury electrode might give better behaviour. Finally, the results of limited ^{1}H-NMR studies are shown in Table 21.

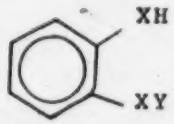
Table 21: ^{1}H-NMR Spectra[a]

Compound	Solvent	NCH_2	NCH_3	aromatic
$[(C_2H_5)_4N]_2Ti(OSC_6H_4)_3$	CD_3CN	3.00 (16H,q)	1.05 (14H,tt)	6.1-7.0 (12H,m)
$[(C_2H_5)_4N]_2Ti(O_2C_6H_4)_3$	CD_3CN	3.12 (16H,q)	1.15 (24H,tt)	5.9-6.5 (12H,m)

[a]Key: tt,triplet of triplets; q,quartet; m,complex multiplet; intensities shown in parentheses.

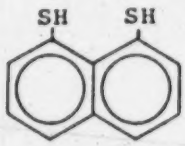
CHAPTER 5: COMPLEXES OF NAPHTHALENE-1,8-DITHIOL

In Chapters 2 and 4 a new synthetic route was presented for the synthesis of metal complexes with ligands of the type;



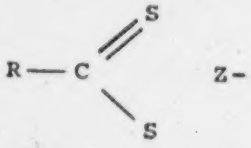
(I)

where X and Y are O or S. In this chapter the extension of this route to complexes of ligands of the type:

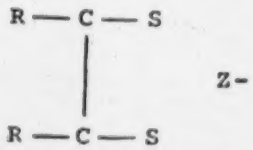


will be presented.

While the chemistry of metal complexes of mono[129,130] and dianionic ligands ligands[114,129,131,132] of types III and IV



(III)



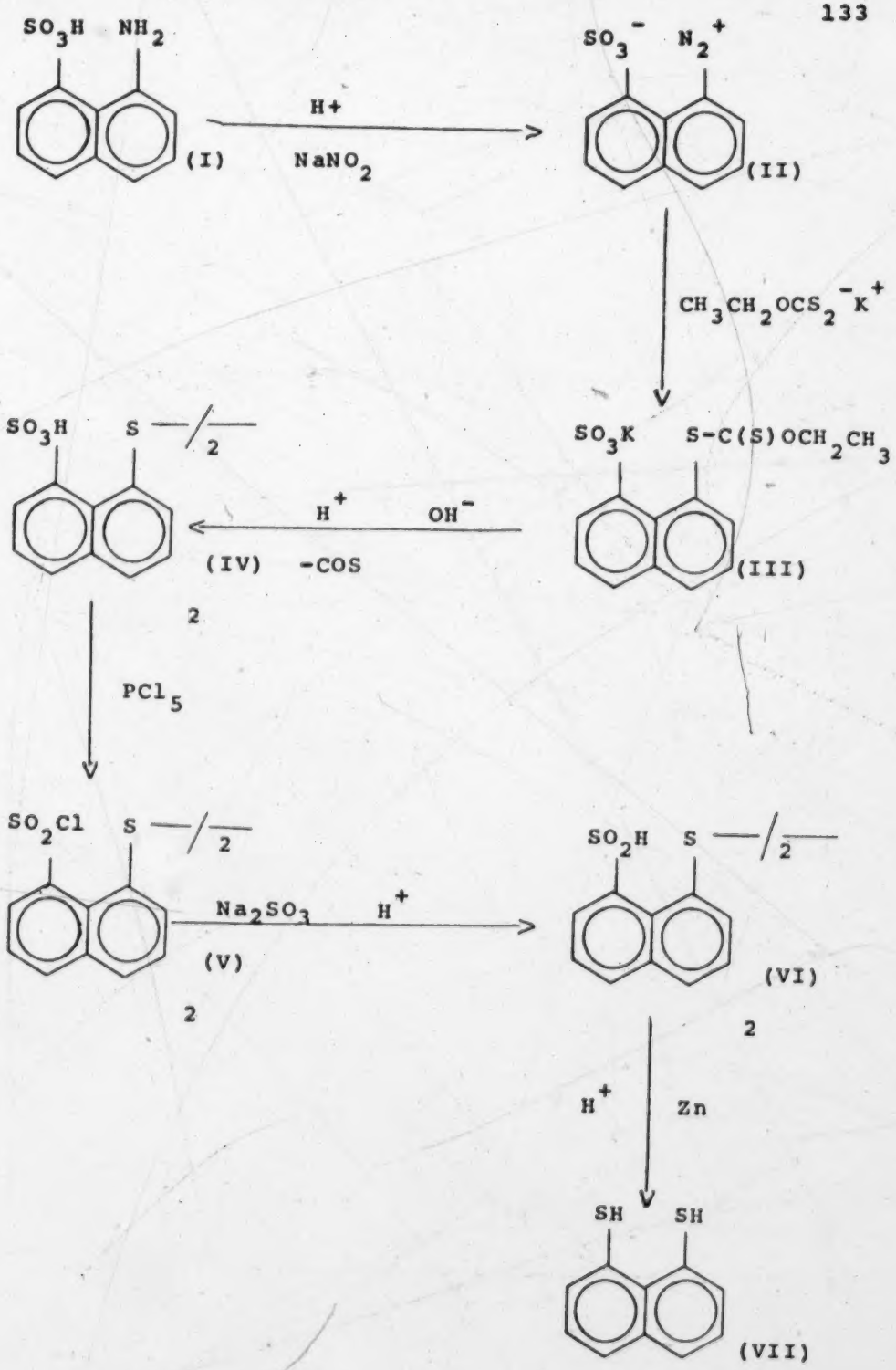
(IV)

have been the subject of a large number of investigations, the 1,3-dithiolates seem to have attracted little attention, with the only report being that of some 2 to 1 complexes of hexachloronaphthalene-1,8-dithiol with Ni, Pd, Pt and Zn.[133] The complexes presented here represent the first example of 3 to 1 naphthalene-1,8-dithiol complexes, having the formula $[(C_2H_5)_4N]_2M(S_2C_{10}H_6)_3$, where M is Ti, Zr, or Hf.

Experimental

The general procedures used in the preparation of these complexes have been outlined in Chapter 2. Naphthalene-1,8-dithiol was prepared by a published procedure,[134,135] scheme 14, given here with slight modification.

In a 3ℓ, 3-neck flask fitted with a mechanical stirrer was placed 466 g of Eastman technical 8-aminonaphthalene-1-sulfonic acid(I), 490 ml of water and 490 ml of concentrated HCl. The resulting suspension was cooled to 0° C in an ice-methanol bath and a solution of 153 g of $NaNO_2$ in 280 ml of water was added dropwise over a period of 3 hours keeping the temperature between 0 and 5° C. At the end of this time, severe foaming occurred and addition was stopped, but stirring at 0-5 °C was continued for 1½ hours. The solution was then filtered through a large Büchner funnel and the tan solid (II) was vacuum dried and separated into seven equal portions of 76 g which were then treated in the following manner. In a well ventilated hood in a 2ℓ beaker equipped with a nichrome wire stirrer (be sure to use nichrome wire)[136] was placed 60 g of technical potassium ethylxanthate in a solution of 20 g of


SO3H NH2
(I)
H+
NaNO2
SO3- N2+
(II)
CH3CH2OCS2-K+
SO3K S-C(S)OCH2CH3
(III)
H+ OH-
(IV) -COS
SO3H S
2
2
PCl5
SO2Cl S
2
Na2SO3 H+
(V)
2
SO2H S
2
(VI)
2
H+ Zn
SH SH
(VII)

(14)

Na_2CO_3 in 120 ml of water. The diazosulfonate(II) prepared above (76 g) was suspended in 120 ml of ice-water and added carefully to the solution above, which was being kept at 50-55° C. The reaction mixture turned dark brown and N_2 was evolved vigorously. When N_2 evolution had ceased, 300 g of a 30% aqueous NaOH solution was added slowly and the resulting mixture was heated to 90° C. After being held at 85-90° C for 20 min., the mixture was boiled for 20 minutes and concentrated to about 500 ml. The solution was carefully acidified with 550 ml of 6M HCl resulting in COS evolution. After cooling overnight, a yellow solid was collected by filtration in a yield of 55 g. The disulfide(IV) must be thoroughly dried before the next step. Total yield 350 g.

In a 1ℓ, 3-neck flask fitted with a stirrer and thermometer, was placed 100 g of the thoroughly dried disulfide(IV) prepared above. While cooling in an ice bath, 150 g of $POCl_3$ was added with resulting heat evolution. The mixture was cooled to 10° C in an ice bath, and 120 g of PCl_5 was added from a Schlenk tube over a period of 1/2 hour while the

reaction mixture was kept below 15° C. The reaction mixture was stirred and cooled for an additional 2 hours and then poured over 1200 g of ice in a 2ℓ beaker cooled in ice. A great deal of heat was evolved and the resulting mixture was cooled with occasional stirring for 1/2 hour. The dark brown solid(V) was collected on a Büchner funnel and although wet was converted directly to the sulfinic acid(VI).

The crude product was added to 128 g of Na_2SO_3 in 1ℓ of boiling water, and the mixture was boiled for 10 minutes. After cooling, the solution was filtered and finally acidified with 6N H_2SO_4 to pH 3. The milky mixture resulting was cooled in ice and the solid filtered off. Yield 50 g of the sulfinic acid(VI).

The reduction of 33 g of 1,1'-dithionapthalene-8,8'-disulfinic acid(VI) was carried out under N_2 atmosphere in a 2ℓ, 3-neck flask fitted with a condenser and mechanical stirrer. To the sulfinic acid was added 1ℓ of 98% ethanol and 500 ml of concentrated HCl and the mixture was heated. From a Schlenk tube, 165 g of Zn dust was added carefully over a period of 1/2 hour and the resulting solution was refluxed for 1/2 hour. The solution was filtered hot through an 11 cm, 10-20 μ glass frit and the zinc residue was washed with boiling 98% ethanol. The

product was vacuum dried to yield 21 g of pale, yellow flakes. When prepared in this manner the product is well-behaved and air stable for more than the time necessary for weighings, but was nonetheless stored under nitrogen.

Lithium cyclopentadienide was prepared by reaction of a filtered solution of n-butyllithium (Matheson, Coleman and Bell) with excess cyclopentadiene at -78^0 in hexanes. The mixture was gradually warmed to room temperature and the white product was filtered off, washed with hexanes, and vacuum dried.

$Li_2S_2C_{10}H_6$

The dilithium salt of naphthalene dithiol was prepared by adding a stoichiometric amount of lithium cyclopentadienide, in THF, to naphthalene-1,8-dithiol in THF. The solvent was stripped off, and an IR was run on the solid. The product was not purified and was only used for IR and UV spectra.

Preparation of the Complexes

$[(C_2H_5)_4N]_2\ Ti(S_2C_{10}H_6)_3$

Lithium cyclopentadienide, 0.305 g (0.00424 mole), in 20 ml of THF was added to 0.817 g (0.00424 mole), of naphthalene-1,8-dithiol in 30 ml of THF resulting

in the formation of a yellow solution. Next, 0.410 g (0.00106 mole) of tetrakisdiethylamidotitanium was added in 30 ml of THF. With the addition of the first drop of the Ti solution, the reaction mixture turned burgundy-black and remained so throughout the addition. After stirring overnight, 1.09 g (0.00424 mole) of tetraethylammonium iodide, which had been dried at 100° C and 0.05 mm Hg for 15 hours, was added directly to the reaction mixture. The THF was then pumped off and the residue was washed twice with 50 ml of dry ether. After thorough drying, 150 to 200 ml of CH_3CN was added and the mixture was heated to near boiling, then filtered hot. The filtrate was cooled overnight in a refrigerator yielding black needles which were collected by filtration and vacuum dried. Yield 0.603 g, 65% based on Ti, mp 211-212° C under vacuum. Anal. Calcd: C, 62.84; H, 6.65; N, 3.19; S, 21.88; Ti, 5.45. Found: C, 61.10; H, 6.33; N, 3.99; S, 21.83; Ti, 5.56.

In a manner similar to that used for Ti, the Zr and Hf complexes were isolated using either a 4 to 1 or 3 to 1, ligand to metal ratio.

$[(C_2H_5)_4N]_2Zr(S_2C_{10}H_6)_3$

Orange platelets were obtained in 30% yield,

decomp. 199° C under vacuum. Anal. Calcd: C, 59.89; H, 6.34; N, 3.04; S, 20.85. Found: C, 58.05; H, 6.17; N, 3.42; S, 20.17.

$[(C_2H_5)_2N]_2\ Hf(S_2C_{10}H_6)_3$

Yellow platelets were obtained in 22% yield, melting with decomposition at 218-220° C under vacuum. Anal. Calcd: C, 54.17; H, 5.79; N, 2.77; S, 19.05. Found: C, 51.90; H, 5.81; N, 2.77; S, 20.01.

Results

Complexes of naphthalene-1,8-dithiol have been prepared according to the following scheme:

$$M(NR_2)_4 + 2LiSC_{10}H_6SH + C_{10}H_6(SH)_2 \xrightarrow{THF} Li_2M(S_2C_{10}H_6)_3 + 4HNR_2 \qquad (15)$$

where M=Ti, Zr, and Hf.

As in the case of the benzene-1,2-dithiol complexes, the alkali metal salt of the complex was not isolated, but cation exchange was carried out with tetraethylammonium iodide in CH_3CN. However, unlike the benzene-1,2-dithiol complexes, the sodium salts of the naphthalenedithiol complexes were insoluble in CH_3CN. Fortunately, the lithium salts, although

moderately insoluble in CH_3CN, have a high enough solubility for exchange to take place in a reasonable time. The resulting tetraethylammonium salts are slightly soluble in CH_3CN, and moderately soluble in hot CH_3CN thus facilitating isolation of the complexes. For ^1H-NMR purposes, it is necessary to use d_6-DMSO as solvent, and even then an instrument with a good signal to noise ratio is needed. The resulting chemical shifts are shown in Table 22 and the intensities agree with the formulations.

Infrared spectra of the complexes may be compared to that of the ligand and are seen to be consistent with the formulation as tetraethylammonium salts of naphthalenedithiol complexes, Table 23.

Conductivity measurements, Table 24 , are consistent with a 2 to 1 electrolyte in the case of Ti and too high for Zr and Hf.[76] As will later be seen, the Zr and Hf complexes may be undergoing dissociation.

The UV and visible spectra, shown in Table 24 , are clearly dominated by the spectrum of the ligand. Some enhancement of the transitions is seen, but only

Table 22: ^{1}H-NMR Spectra

Complex	Solvent	NCH_2	NCH_3	Aromatic
Ti	d_6-DMSO	3.01 (16H,q)	1.00 (24H,tt)	6.7-7.5 (18H,m)
Zr	d_6-DMSO	3.04 (16H,q)	1.02 (24H,tt)	6.7-7.5 (18H,m)
Hf	d_6-DMSO	3.09 (16H,q)	1.07 (24H,tt)	6.7-7.5 (18H,m)

[a]Key: tt,triplet of triplets; q,quartet; m, complex multiplet; Intensities shown in parentheses.

Table 23: IR Spectra

$[(C_2H_5)_4N]_2Ti(S_2C_{10}H_6)_3$

3040w, 2970w, 2940wsh, 1580w, 1522s, 1475ssh, 1450s, 1408ssh, 1389ssh, 1345s, 1315wsh, 1300msh, 1258vw, 1193vs, 1179ssh, 1169ssh, 1146msh, 1083wsh, 1055msh, 1025msh, 1000m, 878vs, 813vs, 790ssh, 762vs, 631w, 590w, 552m, 450s, 320s.

$[(C_2H_5)_4N]_2Zr(S_2C_{10}H_6)_3$

3030vwsh, 3000vwsh, 2970w, 1582w, 1525m, 1472s, 1447msh, 1432msh, 1421m, 1388m, 1360msh, 1345s, 1258m, 1192s, 1183ssh, 1170ssh, 1140msh, 1088s, 1052ssh, 1018ssh, 997s, 874sm 814vs, 785ssh, 763s, 723wsh, 629w, 587vw, 545w, 483wsh, 455msh, 435s, 425msh.

$[(C_2H_5)_4N]_2Hf(S_2C_{10}H_6)_3$

3040vwsh, 2970w, 1582w, 1531s, 1477s, 1450msh, 1433msh, 1415s, 1390s, 1367msh, 1348m, 1318w, 1298m, 1263m, 1199s, 1174s, 1150msh, 1110m, 1057m, 1002s, 986msh, 879s, 816s, 810ssh, 802msh, 789msh, 769s, 747m, 613w, 622w, 556w, 538w, 526w.

$Li_2(S_2C_{10}H_6)$

3040vwsh, 2970w, 1600w, 1536s, 1484w, 1414m, 1351m, 1299w, 1262w, 1209m, 1195s, 1147w, 1097s,

Table 23 continued

1046s, 1022ssh, 983w, 900wsh, 874m, 813ssh, 802s,

763s, 722w, 622vw, 547.

$(SH)_2C_{10}H_6$

3050w, 2560msh, 2530m, 1599w, 1549m,

1498w, 1418w, 1365m, 1337vwsh, 1315m, 1213s, 1064vw,

985m, 937m, 901vw, 896vw, 867m, 814ssh, 811s,

784vw, 757s, 720m, 580w, 530vw, 467vw.

Table 24: Conductivity[a] and UV-Visible[b]

Compound	Λ_m[c]	Maxima (cm^{-1}) and Intensities (ε)
$[(C_2H_5)_4N]_2Ti(S_2C_{10}H_6)_3$	227	21,400(12,000); 25,600 (29,000)sh; 27,300 (30,400).
$[(C_2H_5)_4N]_2Zr(S_2C_{10}H_6)_3$	350	27,300(49,600); 40,000(102,000)sh
$[(C_2H_5)_4N]_2Hf(S_2C_{10}H_6)_3$	308	27,500(38,300); 40,000(83,600)sh
$Li_2S_2C_{10}H_6$		27,500(12,300); 40,500(28,000)sh

[a] Solutions approx. 10^{-3} M in CH_3CN

[b] Solutions approx. 10^{-4} M in CH_3CN

[c] $cm^2\ ohm^{-1}\ mole^{-1}$

Ti appears to have a pronounced metal-ligand interaction.

Some mention must also be made of the analytical data of the compounds. The complexes have consistently displayed low carbon analysis, and the total of all elements analyzed is less than 100% in the Ti case. Obvious sources of contamination involve Li or I, but tests for both of these elements have been negative. Another possible contaminant is moisture, but not only have the complexes been handled under inert atmosphere, but IR data show an absence of any hydrolysis products. While it cannot be stated with all certainty that the complexes are pure, the evidence that we have suggests that some problem may be involved in the carbon analysis. In any event, the nature of the complexes has certainly been established and at this time it seems that no other synthetic routes are available to provide a way of preparing the complexes, especially in an unquestionably pure state. Further experimentation is needed to clarify this question.

Discussion:

Complexes of naphthalene-1,8-dithiol are interesting for at least two reasons. Firstly, it is interesting

to ponder whether this ligand will form highly delocalized bonds with metals as the 1,2-dithiolenes do, or whether it will behave more like the dithiocarbamates. The classification of ligand systems as "even" or "odd" according to the number of orbitals available for π -bonding within the ligand clearly distinguishes between the 1,2-dithiolenes and 1,1-dithio acids.[30] However, naphthalene-1,8-dithiol presents a small problem in that it is "even" but it is still not possible to write favorable resonance structures for the dithioketone form. The whole question has been clarified by Eisenberg when he points out that one must consider the symmetry of the appropriate ligand molecular orbitals.[32] That is, the ligand orbitals must not only be of the proper energy for π -bonding to the metal, as reasoned in Chapter 2, but also must have the appropriate symmetry. Molecular orbital calculations by Birss on the benzene-1,2-dithiolato, Figure 13, and napthalene-1,8-dithiolato, Figure 14, ligand system clearly show that the naphthalene-1,8-dithiolato ligand has a highest filled molecular orbital of a_2 symmetry which, unlike the benzene dithiolato ligand, is not the

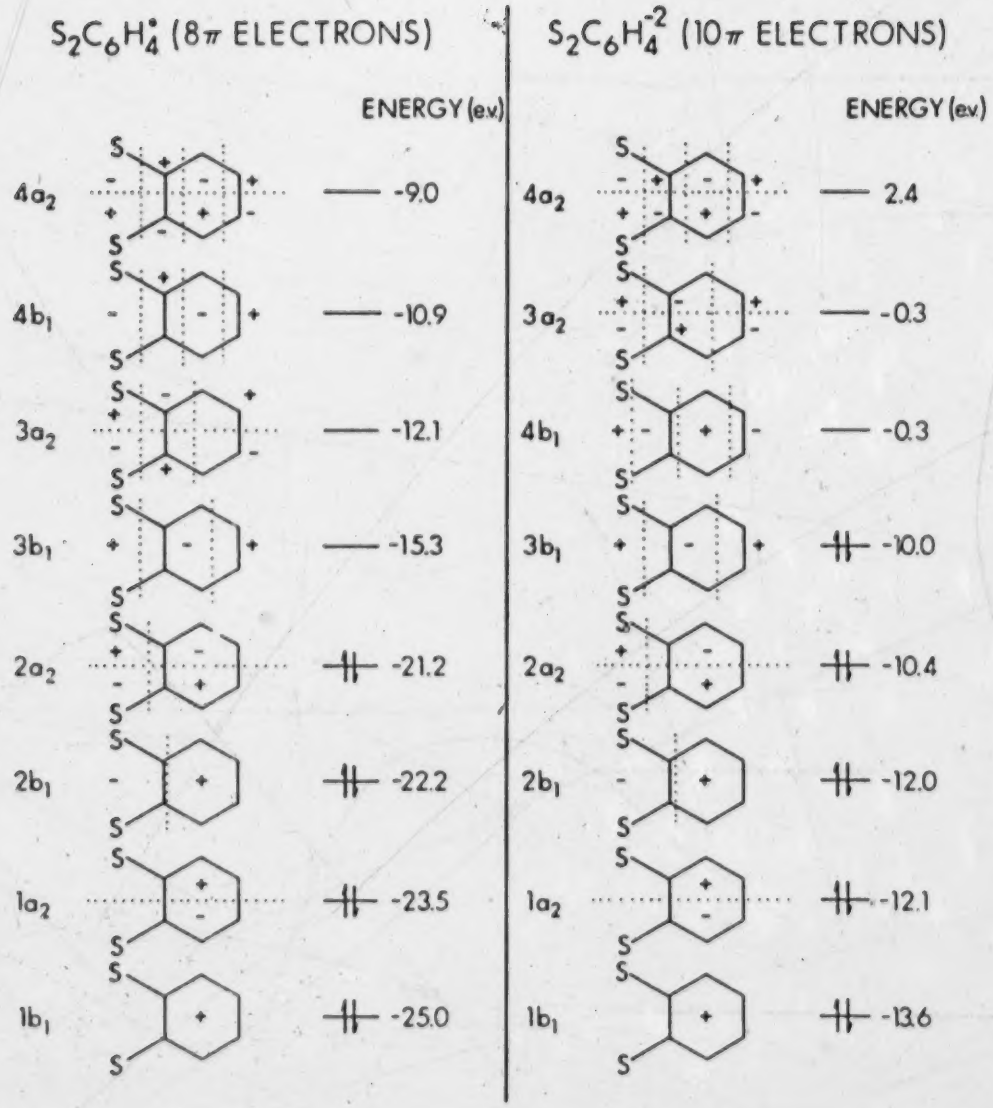


Figure 13: A Diagram of the π-System Molecular Orbitals of Benzene-1,2-dithiolate.

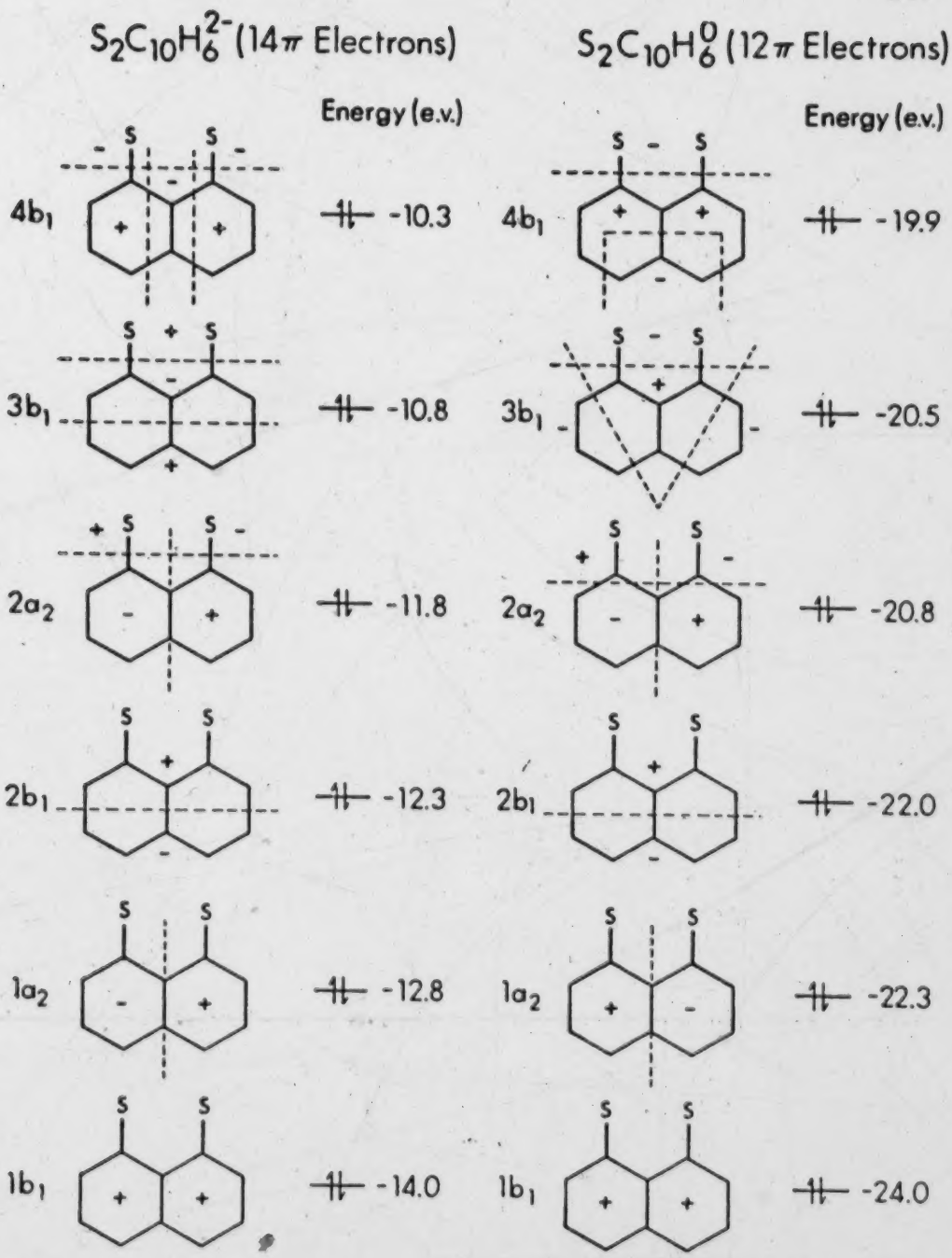
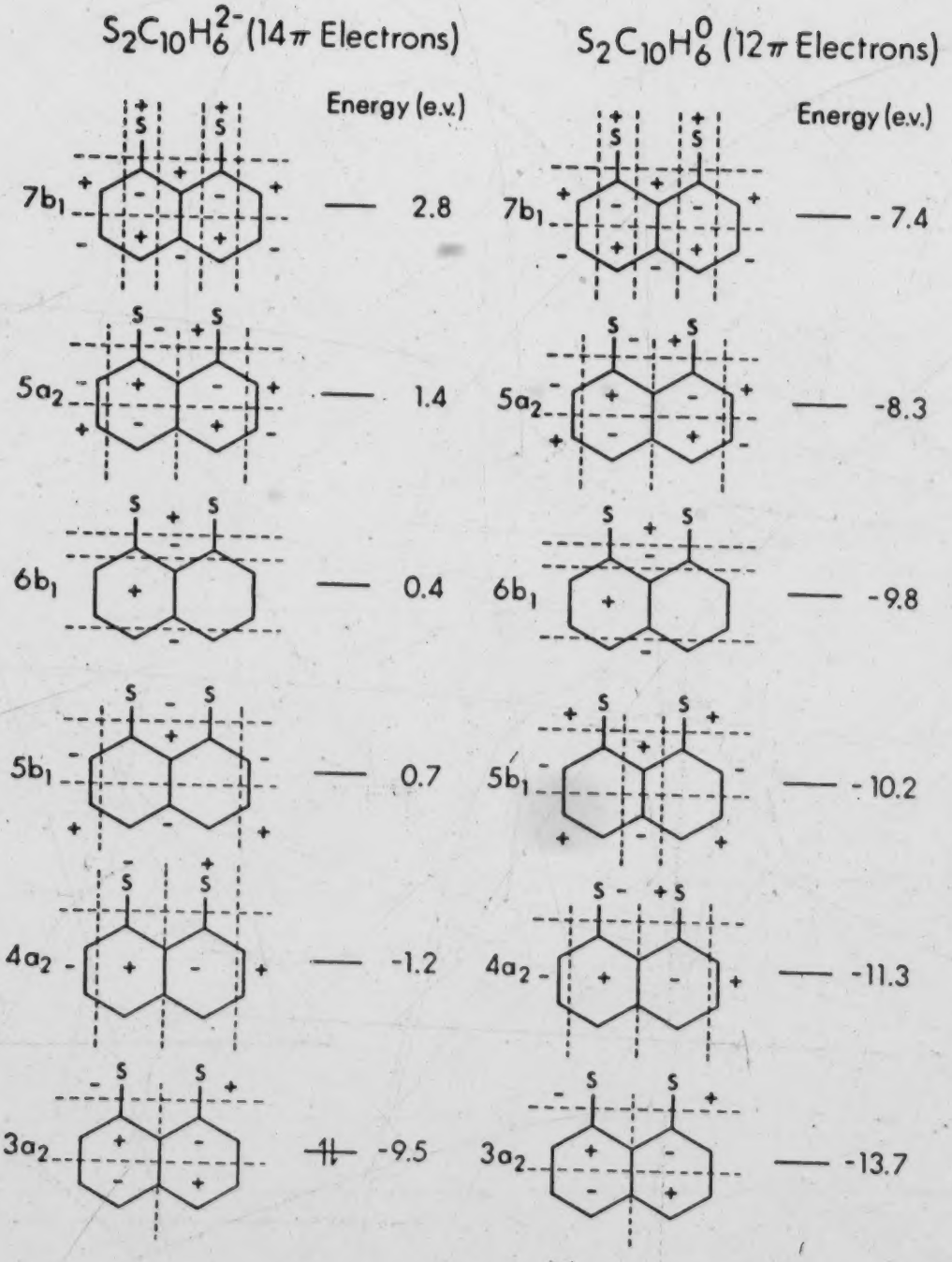


Figure 14: A Diagram of the π-System Molecular Orbitals of Naphthalene-1,8-dithiolate.


$S_2C_{10}H_6^{2-}$ (14π Electrons)
Energy (e.v.)
7b1
2.8
5a2
1.4
6b1
0.4
5b1
0.7
4a2
-1.2
3a2
-9.5
$S_2C_{10}H_6^{0}$ (12π Electrons)
Energy (e.v.)
7b1
- 7.4
5a2
-8.3
6b1
-9.8
5b1
- 10.2
4a2
-11.3
3a2
-13.7

appropriate symmetry for effective π-bonding with the metal.[138] On the other hand, if σ -bonding is the important factor in favoring trigonal prismatic geometry, then the naphthalene-1,8-dithiolate complexes should certainly behave more like benzene-1,2-dithiolate complexes. For σ -bonding, the distinction between "even" and "odd" ligands systems would apparently not exist. However, a distinction between mono and dianionic ligands would certainly be important since the dianions would be stronger σ -donors. At the same time, the distinction between "even" and "odd" ligands would still have to be retained when considering the electrochemical behavior of the complexes. Unfortunately, the evidence that we have at this time does not provide a good test for the various theories. It has already been shown, Chapter 2, that the benzene-1,2-dithiol complexes of Ti, Zr, and Hf behave like metal dithiolates and show few of the unusual characteristics associated with metal dithiolenes. Thus, it is not surprising that the corresponding naphthalenedithiol complexes also behave as dithiolates. However, it is also evident that the naphthalene dithiol ligand is not as strongly bound as benzenedithiol with these metals,

both from the higher energy UV spectra, and also from the instability of the Zr and Hf complexes. The conductivity, UV spectra, and air sensitivity of the Zr and Hf complexes all suggest that only weak bonds are being formed with the metal in contrast to the air stable Ti complex. Whether such differences will be evident in other complexes remains to be seen.

A second reason for studying complexes of naphthalene-1,8-dithiol, and in particular those described here, arises from the small bite expected for this ligand. Although no structural work has been carried out on this ligand, rough calculations predict a bite of ~2.4 Å. Using a Ti-S bond length of ~2.4 Å,[45,46] one then arrives at a normalized bite of 1.0.[83] Such a small normalized bite has been predicted to give near trigonal prismatic complexes in order to minimize ligand-ligand repulsions.[83] As of yet no 3 to 1 chelates with such a small bite have been reported. Rather, other ligands with small bites such as NO_3^-, tropolone, or dialkyldithiocarbamates give rise to eight coordinate complexes with the early transition metals.[139,140] Possibly the high charge of the

naphthalenedithiol ligand favors low coordination numbers. Attempts were also made to synthesize eight coordinate naphthalene dithiol complexes by using 4 to 1 ligand to metal ratios, however, both these conditions and 3 to 1 ratios resulted in 3 to 1 complexes. Whether these 3 to 1 complexes are trigonal prismatic will require further investigations. Work is also needed in the area of complex formation with other metals and with other ligand systems such as ethane-1,2-dithiol to assess the relative roles of σ and π-bonding.

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95. The function being minimized was $\Sigma w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors respectively and $w = (\sigma F_o)^{-2}$.

96. Scattering factors for the neutral atoms were used as tabulated by Cromer and Mann[98] for Ta, S and C and Stewart, Davidson and Simpson[99] for H.

97. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ while $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, w, F_o and F_c are as previously defined.[95]

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